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—OF THE—

American Ceramic Society

A Monthly Journal devoted to the Arts and Sciences Related to the Silicate Industries.

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JOURNAL
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AMERICAN CERAMIC SOCIETY

A monthly journal devoted to the arts and sciences related to the silicate industries.

Vol. 1 **April, 1918** **No. 4**

EDITORIALS.

THE PRESENT UNUSUAL DEMAND FOR MEN WITH TECHNICAL CERAMIC TRAINING.

Probably the best known of the trite sayings of Andrew Carnegie is the admonition to "put all your eggs in one basket and watch that basket" but another which has enjoyed a very wide circulation is the advice given to a business friend which was, in substance, "If you have a hundred thousand dollars to spend on the development of a new proposition, spend the first fifty thousand in finding out what is already known."

Twenty years ago, or at about the time the American Ceramic Society was formed, it was in rare cases only that any systematic attempt was made to find out in advance of embarking upon a new proposition or of attempting to develop some new product or new manufacturing process, what successes or what failures had accompanied similar earlier experiences in attempting to accomplish the same or similar results and it was almost never that a systematic attempt was made to determine in advance what laws of nature, chemical or physical, were to be met with in carrying out the undertaking and what influences such laws must have in determining the limitations under which the work must be done.

Today the situation is very different. The evolution has been almost a revolution. The old methods of secrecy and distrust and ignorance have given way to frank discussion and to more than a beginning of real knowledge in the science of silicates. As an integral part of this evolution (or revolution) has come the

establishment and growth of departments in our institutions of learning devoted to the study of the fundamentals underlying all processes of silicate manufacturing and the dissemination throughout the industry of the knowledge thus accumulated.

This evolution has borne fruit abundantly. With it there has come an ever-increasing demand for men with suitable training, capable of taking their places in the manufacturing industries. This demand is felt in all branches of the silicate industries—in the clayware industries, in glass plants, in cement mills, in enameling plants and in the many allied manufacturing establishments.

With this logical development of the industry along normal lines has come the added stimulus of war demands. One feature of the very unusual situation created by the world war is the necessity that has arisen in many branches of the Ceramic Industries, in common with almost all other manufacturing industries, of replacing with materials of domestic origin or of domestic manufacture, materials which were formerly imported. Such importations have been cut off either because imported articles formerly came from the enemy countries or because the great demand for shipping facilities for purely war purposes has made it impossible to continue shipments of materials which could be duplicated at home. It has taken a tremendous amount of investigation and research, both theoretical and practical, to accomplish the substitution of suitable domestic materials for the former imported articles.

Another special demand upon the Ceramic industries is that for new products and improved forms and qualities of old products made necessary by the new demands of a war business. The Nation's business is, and has been for a year and a half, the business of War and products demanded by the new manufactures incident thereto have had to be made. New knowledge and new experience have been most essential in meeting the new difficulties involved.

With a careful analysis of the situation at hand, it is not difficult to understand the present great demand for men trained in the sciences upon which the silicate industries are founded. Our institutions of learning report very heavy demands for men, and these demands they are quite unable to satisfy with the com-

paratively small number of men undergoing such training. From the larger public and private laboratories interested in the silicate work come the same reports of numerous demands for trained men. The demand far exceeds the supply. It cannot be denied that this situation of heavy demand and limited supply has been responsible for the fact that training has not always been as complete as it should have been, but very great strides have been made, within the past decade especially.

The calling is one offering a very attractive future in the interesting nature of the work, in the possibilities of development, and in remuneration and there can be no doubt that in proportion to the increase in a general realization of this situation will come an increase in the number of young men who fit themselves to supply this demand by entering our colleges and universities to gain the required training in the scientific courses dealing with ceramic work.

AMERICAN CERAMIC SOCIETY AT THE FOURTH NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The American Ceramic Society will be represented at the Fourth National Exposition of Chemical Industries to be held at the Grand Central Palace, New York City, the week of Sept. 23rd.

The participation of the Society in the Exposition of last year evidenced an unusual interest in ceramic work and this year the Exposition management has arranged for the grouping of the ceramic exhibits in a Ceramic Section. The American Ceramic Society will have its headquarters in this Section.

The Ceramic industry includes that branch of the chemical industry engaged in the production and manufacture of silicates. Including as it does a group of industries producing materials and wares to the value of hundreds of millions of dollars, it is one of the largest single branches of manufacture based upon chemical technology.

Although the public at large has perhaps appreciated the recent progress made in other branches of the chemical industry,

such as in the manufacture of dyes and munitions, it does not have a thorough realization of the extent of the ceramic industries nor of their basic importance to the so-called "essential industries." The war essential nature of some of the products which are being produced by this group of manufacturers should also not be overlooked.

Among the ceramic products which are vitally necessary to the successful manufacture of other essential products we would mention fire brick, furnace linings, flue linings, crucibles, retorts and other REFRACTORIES used in the production of iron, steel, brass, copper and other metals and their alloys; ABRASIVES for the grinding of optical products, munitions, machine parts, etc.; CHEMICAL PORCELAIN AND STONEWARE for the production of acids, heavy chemicals, explosives, etc. PORTLAND CEMENT for ships, building construction, etc.; BUILDING AND CONSTRUCTION MATERIALS as brick, tile, fire-proofing, terra cotta, conduits, sewer pipe, drain tile, etc., necessary for the construction of Government buildings, ordnance storehouses, training camps, etc.; and ENAMELED IRON WARE used in the manufacture of chemicals, explosive products, etc., and very extensively for the serving of food in both the Army and Navy.

The Ceramic Industry has also been called upon to develop and produce certain military products of a vitally essential nature and which were imported into this country previous to the war. Among these should be mentioned OPTICAL GLASS for gun sights, range finders, periscopes, etc.; SPECIAL GLASS for searchlight reflectors, ships' lights, etc.; SPARK PLUGS for airplane engines; IMPROVED REFRACTORIES for the furnaces of destroyers and other battle craft; and LABORATORY GLASSWARE AND PORCELAIN for experimental and control work in the chemical industries.

The Ceramic Section at the coming Fourth National Exposition of Chemical Industries will undoubtedly awaken the interest—not only of those engaged in the production of ceramic wares—but also of many of the engineers, chemists, superintendents and others in attendance and in whose work imporant use is made of Ceramic products.

ORIGINAL PAPERS AND DISCUSSIONS.

THE EFFECT OF THE DEGREE OF SMELTING ON THE PROPERTIES OF A FRIT.

By E. P. Poste and B. A. Rice, Elyria, Ohio.

Introduction.

In a consideration of the actual composition of a frit, we assume that certain constituents entering into the raw mixture pass through chemical changes which bring about the volatilization of certain portions and the fusing together of the remaining ingredients into a homogeneous mass having a certain definite chemical composition. This we express in terms of the melted oxides or by means of the molecular formula. Not only is this assumption made relative to the enamel frits, but it also finds application in connection with fritted glazes, glasses and various other ceramic products which result from the use of mixtures of such materials as soda, feldspar, borax, fluorspar, etc.

Upon reading the literature on the subject of the chemistry of frits, we find that the above general conditions are taken for granted; we do not find a report of an investigation leading to a comparison between the actual composition of the resulting frit and the theoretical composition as shown by the computed formula.

If we assume that, at some particular stage in the smelting of an enamel, the actual composition corresponds to the theoretical composition, there must be two stages, one on either side of this particular point, during the first of which there are still present some of the materials which are volatile in the ordinary sense of the term, and beyond which point further heating may possibly cause decomposition and volatilization of some of those materials which we ordinarily consider as being non-volatile.

Some months ago, a series of experiments was started which has thrown considerable light on this particular subject and the results may be of sufficient interest to others engaged in the ceramic industries to warrant the presentation of this paper.

Experimental.

The work has included the melting of a commercial enamel formula under conditions covering a large variation in the time of smelting. The enamel thus produced has been studied, not as to its behavior when applied to the ware, but as to the chemical and physical changes which have been brought about by the different degrees of smelting. Samples of each have been analyzed and the results compared with the theoretical composition of the frit. Deformation tests have been made in order to determine the effect of the various degrees of smelting upon the deformation behavior of the resulting frit. Tests to determine the effect of the varying heat treatments on the resistance of the enamels to acids have also been made.

As to the formula used, it will be sufficient to state that it was fairly resistant to acids and prepared from the usual enamel constituents. We can draw definite conclusions in a relative manner without stating the formula of the enamel or the actual analyses of the resulting frits.

The raw materials, properly mixed, were placed in a tilting smelter which had been pre-heated in the usual manner. As soon as the material had reached a fairly uniform condition of fusion and after thorough stirring, a small portion of the enamel was withdrawn from the smelter—the total time required to reach this condition being taken as unity. This enamel was designated as "A." In like manner samples were poured from the smelter at the following time intervals based on the former as unity: $1^1/_2$, 2, $2^1/_2$, 3 and $3^1/_2$, the samples being designated A, B, C, D, E and F, respectively.

The samples thus prepared were thoroughly dried and uniformly ground dry, without mill additions, in an experimental pebble mill. That portion of the resulting powder passing a 200-mesh sieve was used as the basis of the three following tests:

1. Chemical Analyses.

The chemical analyses of the six samples were made in the usual manner. The scheme outlined by Landrum[1] proved very helpful in this work. Mellor's Treatise on the Ceramic Industries, Vol. 1, proved a most reliable guide.

2. Deformation Test.

A portion of the 200-mesh powder was mixed with water and an organic binder and molded into test cones of standard dimensions. The cones were thoroughly dried and mounted in pairs on a piece of asbestos board. This mounting was placed in an electric furnace (at a temperature of 600° F.) in such a manner that the junction of a thermocouple was just between the two cones. The temperature of the furnace was gradually increased at a uniform rate and two points noted. The first of these was the temperature at which the tip of the cone was first observed to move and the second, the temperature at which the tip of the cone was just touching the asbestos board upon which the cones were mounted. By noting both cones in this manner and taking the average temperature at which they were first observed to deform and at which they were touching, two readings were obtained, the first of which was termed the starting point and the second, the deformation point. The term "Deformation range" has been applied to the interval existing between these two temperatures and has been considered as indicating the general range through which the enamel is in a semi-fused condition but still sufficiently viscous to remain in place.

3. Acid Test.

The acid test was made on the 200-mesh powder in accordance with the methods which have been previously worked out and reported.[2] The method in brief is as follows:

Two grams of the frit were carefully weighed in a 400 cc. beaker, to which was added 100 cc. of the desired solution (10 per cent. hydrochloric acid in this case).

[1] *Trans. Am. Ceram. Soc.*, **12**, 144 (1910).

[2] *Ibid.*, **17**, 137 (1915); **18**, 570 (1916); **19**, 146 (1917).

The contents of the beaker were thoroughly stirred, covered with a watch glass and then allowed to stand at the laboratory temperature for 24 hours. The remaining frit was then washed into a weighed Gooch crucible, all traces of acid removed, the crucible dried and weighed, and the loss of weight determined. This loss of weight was taken as the acid loss under these conditions. In this manner, by running a series of tests under parallel conditions, a very good comparison results. Obviously, the actual temperature has an effect on the results but under these particular conditions the results are comparative as the same temperature has existed during all of the tests.

Chemical Analyses: Results.

As to the actual analyses of the six samples—the first step was to determine whether fluorine was present in the frit as a considerable quantity of fluorspar had been used in the raw batches. Thorough qualitative tests did not detect the presence of fluorine. This fact is interesting in view of the statement made by Landrum[1]—"In a ground coat enamel for sheet steel, where the frits are properly fused, the fluorine from the calcium fluoride entirely disappears. In white enamels, however, when cryolite is added as an opacifier, the melting is not carried so far and fluorine does remain in the enamel." The enamel in question contains no cryolite and the fluorine from the fluorspar was all volatilized—even in the first sample which had been smelted to a lesser degree than it would be in the production of an ordinary commercial frit from this formula.

An appreciation of the results of these analyses can be had by a consideration of the SiO_2, Al_2O_3, B_2O_3, CaO, K_2O, and Na_2O contents. There were other ingredients present in small quantities in the enamels but their fluctuations throughout the series are not important.

In Table I we have taken the theoretical composition of the enamel as a standard and have indicated the excess or deficiency of SiO_2, Al_2O_3, B_2O_3, CaO, K_2O and Na_2O as related to the theoretical amounts. For instance, in enamel "A" there was present

[1] *Trans. Am. Ceram. Soc.*, **14**, 544 (1912).

3.88 per cent. less of SiO_2 than is called for in the theoretical formula while in "B," there was 0.46 per cent. more.

TABLE I.[1]

	A.	B.	C.	D.	E.	F.
SiO_2.....	—3.88	+0.46	+1.32	+2.56	+4.62	+7.92
Al_2O_3.....	+0.51	+0.40	+0.50	+0.45	+0.62	+0.80
B_2O_3.....	—0.10	—1.80	—2.90	—3.20	—4.20	—6.00
CaO.....	+0.73	+0.52	+0.37	+0.35	+0.30	+0.17
K_2O.....	+1.63	+1.10	+1.00	+0.43	+0.40	+0.26
Na_2O.....	+1.18	+0.18	—1.22	—1.93	—2.50	—2.77

A graphical interpretation of these results is very interesting. In Fig. 1 we have considered the horizontal line at the center of the chart to indicate the actual determination corresponding

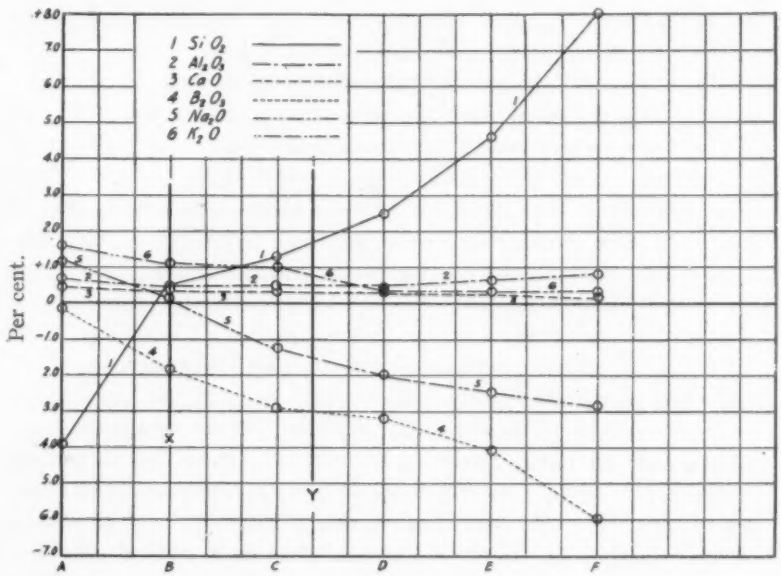

FIG. 1.

to the theoretical value. If the analysis value exceeds the theoretical amount, it has been designated by a position above the horizontal line, and if the figure has been below the theoretical

[1] In three cases the values here reported are slightly different from the analytical data—modified to be consistent with the balance of the data.

amount, it has been placed below the line. The horizontal distances AB, AC, AD, AE and AF, indicate the time of smelting of each of the respective samples, A being taken as unity.

A study of Fig. 1 leads to certain very definite conclusions. The changes prior to "A" cover the period during which the water is vaporized and most of the nitrates, carbonates and fluorides are decomposed. Beyond "A," a very definite series of changes of another type take place.

It will be seen that the increase in the time of heating has produced a very rapid increase in the percentage of SiO_2 up to "B," after which the rise is very positive but more gradual.

The Al_2O_3 content has not been subject to very marked changes. At "A," it was slightly above the theoretical amount and throughout the series it has at first dropped and then increased gradually and at "F" is somewhat above the value at "A."

The CaO content has slightly decreased from "A" to "F," although always being slightly above the theoretical amount.

The percentage of alkalies has dropped quite materially from "A" to "F" and it is particularly interesting to note that the volatilization of Na_2O has been much more rapid than that of K_2O. In fact, throughout the series there is more K_2O than the theoretical amount, while the Na_2O content drops below the theoretical shortly beyond "B" and at "F" there is a deficiency of nearly 3.0 per cent.

The B_2O_3 content is about equal to the theoretical at "A" and then drops off steadily to "F."

There appears to be a definite point at "B," at which the composition of the entire batch is nearest to that of the theoretical composition—in fact the algebraic sum of the values is practically zero. The line "X" has been drawn through this point on all of the charts. It would seem that the most radical changes, due to the volatilization of substances ordinarily considered as volatile, have come practically to equilibrium at this point. The water has been completely driven off, the nitrates decomposed, the carbonates broken down and the fluorine—with its equivalent of silica—has vaporized as silicon tetrafluoride. In addition to this there has been a noticeable loss in B_2O_3—due to volatilization.

Beyond this line "X" the volatilization of B_2O_3 continues at about the same rate although there seems to be a radical change in the type of the curve for SiO_2 and Na_2O. It is quite apparent that the volatilization of the B_2O_3 and Na_2O is the determining factor in this change and that the increase in the SiO_2 content of the frit is the result.

It is further very interesting to note the point corresponding to the time at which this enamel would normally be poured. The line "Y" has been drawn through this point. We have the following values: SiO_2 +1.7, Al_2O_3 +0.5, CaO +0.3, K_2O +1.9, Na_2O —1.5, and B_2O_3 —3.0. In other words, the frit, as it would normally leave the smelter, is considerably higher in SiO_2, somewhat higher in K_2O, Al_2O_3 and CaO, slightly lower in Na_2O, and very materially lower in B_2O_3 than would be indicated from the theoretical composition obtained from computation.

The data in Table 1 has been calculated on a percentage basis and as is characteristic of data of this kind—a change in the amount of any one constituent, when the actual amount of the others remains constant, makes a difference in the percentage values of the other constituents.

An effort has been made to present the analytical data in a form which will eliminate these objections (Table 2). In doing this we have assumed that, in view of the absence of fluorine in "A," the actual amount of SiO_2 left in the batch through the subsequent stages of the smelting is the same, and that the changes which have taken place have involved the volatilization of other substances.

TABLE 2.

	A.	B.	C.	D.	E.	F.
SiO_2	Assumed constant.					
Al_2O_3	0	—0.56	—0.56	—0.71	—0.73	—0.85
B_2O_3	0	—3.70	—4.95	—5.70	—7.22	—9.50
CaO	0	—0.57	—0.77	—0.89	—1.05	—1.34
K_2O	0	—1.01	—1.19	—1.80	—1.95	—2.31
Na_2O	0	—2.30	—3.73	—3.92	—5.55	—6.30

Assuming that in heating from A to B no change was made in the actual amount of SiO_2, the values for the other oxides have been changed, keeping their ratio to the SiO_2 the same and bring-

ing the SiO_2 to the same actual amount as was indicated in "A." In view of the fact that the percentage of SiO_2 was constantly increasing from A to F, the assumption that the actual weight has been constant has caused a decrease in the actual amounts of the other oxides present. In columns B, C, D, E and F, the actual loss of Al_2O_3, B_2O_3, CaO, K_2O and Na_2O as compared with the actual amounts present in A has been expressed. For instance, in B, assuming that there was no loss of SiO_2, the amount of B_2O_3 is 3.7 points less than was present in A.

In Fig. 2 the data of this table is presented graphically. The line at the top of the chart is designated as zero. The different times of smelting are indicated by A, B, C, D, E and F. The dis-

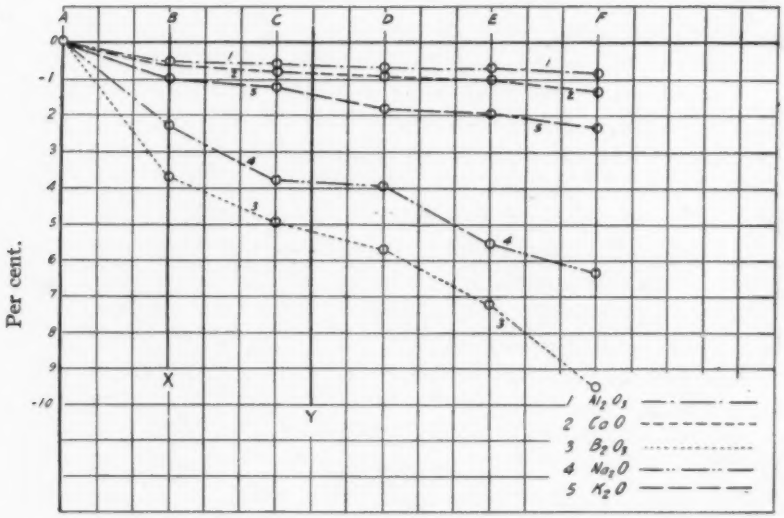

FIG. 2.

tance below the zero line indicates the loss in the amount of the various constituents as compared with the amounts present in A.

From Fig. 2 it will be evident that, on assuming a constant amount of SiO_2 from A on, there has been a gradual loss in the amount of CaO and Al_2O_3, a greater loss in K_2O, and a very material loss in the amounts of Na_2O and B_2O_3. The change in the

direction of the various curves at the line "X" is again quite noticeable.

The above data and curves would indicate that there is a loss of CaO and Al_2O_3 due to the continuous heating from A to F. If this condition is taken as improbable, the data could be rearranged, keeping either the content of CaO or Al_2O_3 constant, in which case the value for the SiO_2 would constantly increase. At the same time there would still be a definite decrease in the amount of B_2O_3 and the alkalies.

As a general conclusion, from the data presented from this point of view, it is quite clear that there is a very marked volatilization of the B_2O_3 and alkalies. Further than this there has been either an increase in the amount of SiO_2 or a decrease in the amount of CaO and Al_2O_3. It hardly seems possible that an absorption of SiO_2 from the walls of the smelter could have taken place and no other source is possible. We therefore conclude that a slight volatilization of the other two oxides took place.

Results: Deformation Tests.

The results of the deformation tests which were made in accordance with the foregoing outline have been rearranged as shown in Table 3. The deformation temperature of A has been taken as a standard and the increase in the deformation temperature above this point is the figure which is given as the value for the deformation temperature of any particular enamel. The deformation range, as given, is the actual temperature interval occurring between the first perceptible tipping of the cone and the final touching of the tip of the cone at the base of the cone mounting.

TABLE 3.

	A.	B.	C.	D.	E.	F.
Deformation Temp..	0° F.	10° F.	30° F.	50° F.	60° F.	80° F.
Deformation Range...	60°	80°	110°	120°	140°	170°

The above figures are readily interpreted by the use of Fig. 3, which shows both the deformation temperatures of the enamels B, C, D, E and F, relative to the deformation temperature of A, and their actual deformation ranges.

A study of Fig. 3 throws some light on the effects of the chemical changes, as indicated by the analyses, upon the physical

properties of the enamels as indicated by the deformation points and deformation ranges. It will be noted that the curve for the deformation temperatures approximates a straight line which rises quite uniformly from A to F, the total increase in deforma-

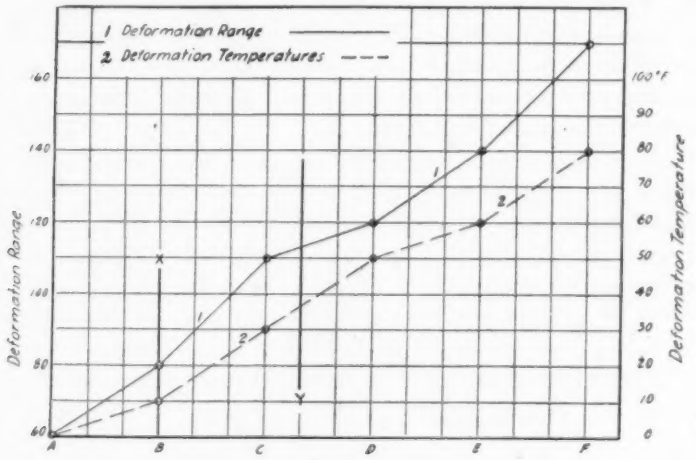

FIG. 3.

tion temperature being about 80° F. The curve for the deformation range is of a very similar nature, showing a range of 60° F. at A and about 170° F. at F.

The observations on both of these curves having been made to the nearest 10°, allowance of this amount for experimental error would make either of these curves very uniform.

There are two additional physical properties of the frit which it will be interesting to take into account. By drawing a hair of enamel from a batch during smelting there is a period during which the hair will contain particles of unfused material and will be quite brittle. As the mass reaches a quiet fusion, the brittleness of this hair greatly diminishes and finally a point of maximum toughness is reached, beyond which it again becomes brittle. For this particular enamel this point of maximum toughness would be crossed by the line "Y" in Fig. 1.

A further observation has to do with the coefficient of expansion of this particular enamel. The theoretical enamel has a coefficient

of linear expansion of 93.7×10^{-7}, calculated by the use of the factors given by Hovestadt.[1] The coefficients of expansion for A, B, C, D, E and F have been computed from the analytical data. These data are given in Table 4 and are plotted graphically in Fig. 4.

TABLE 4.

Coefficient of Linear Expansion.

Theoretical.....	A.	B.	C.	D.	E.	F.
93.7×10^{-7}.....	101.1	96.9	92.3	88.4	88.0	88.2

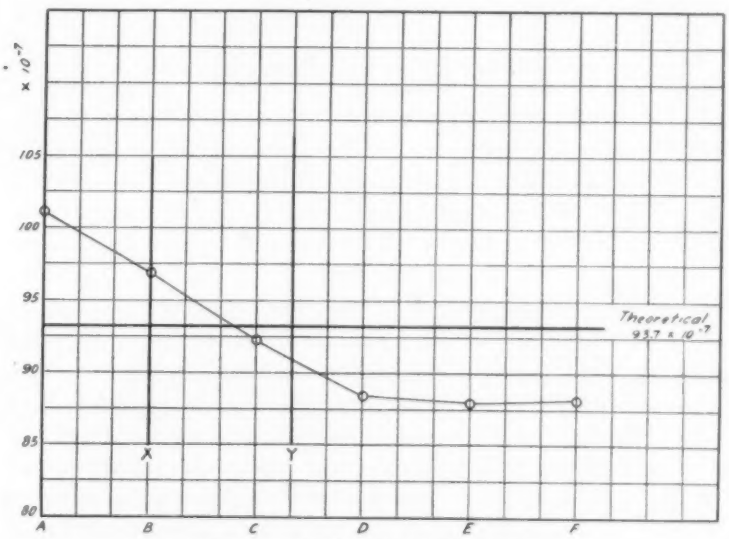

FIG. 4.—Coefficients of expansion.

Results: Acid Resistance Tests.

The tests for acid resistance under standard conditions gave results as shown in Table 5.

TABLE 5.

	A.	B.	C.	D.	E.	F.
Acid loss.....	0.97 g.	0.65	0.57	0.38	0.24	0.14

These figures express the actual acid loss and are the inverse of acid resistance. They are plotted in Fig. 5. It will be noted

[1] Hovestadt (Jena Glass), page 217.

that, although in "A" nearly 1.0 gram of the pulverized frit was dissolved, in F slightly less than 0.15 g. was dissolved, indicating a very marked gain in acid resistance.

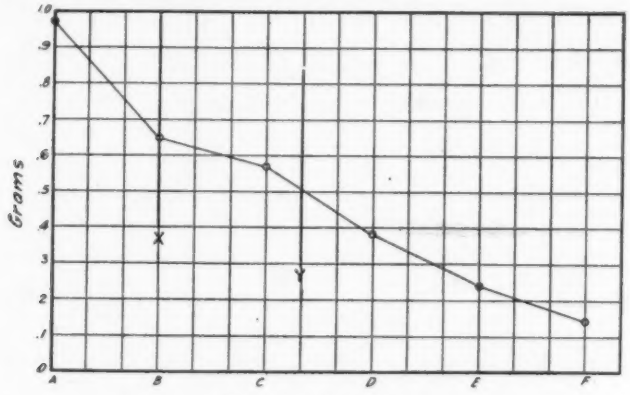

FIG. 5.—Acid loss.

Conclusions.

In general, we may conclude that the chemical composition of a frit at the point of normal pouring may differ quite materially from the composition which would be expected based on theoretical computation. The principal differences in the case at hand are that the SiO_2 content is materially higher, the Al_2O_3, CaO and K_2O are slightly higher, and the Na_2O and B_2O_3 contents are very much lower than the theoretical composition would indicate. Prior to this point the batch as a whole has passed through a stage approximating the computed composition with the exception of the B_2O_3 content. Further heating produces very marked chemical changes which rapidly increase the SiO_2 content and decrease in like manner the content of Na_2O and the B_2O_3, when judged from a percentage point of view. Or, assuming the SiO_2 to remain constant after the volatilization of the silicon tetrafluoride, there is a slight volatilization of CaO, Al_2O_3 and K_2O and very marked losses of B_2O_3 and Na_2O.

As a result of these chemical changes, we introduce an objectionable rise in the maturing point of the enamel but a favorable increase in the deformation range. The computed coefficient of

linear expansion drops quite rapidly and at the end of the series it is no doubt sufficiently low to produce shivering. The enamel would have a marked tendency to over-burn and become very brittle when applied to the ware, were the smelting to be continued very far beyond the line "Y." The further smelting would produce a very desirable increase in the acid resistance of the enamel, but it would appear that the resulting objectionable physical properties would make it impossible to realize this increase in chemical resistance.

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COMMUNICATED DISCUSSION.

J. B. SHAW: Although the results obtained by the authors of this paper could be more simply expressed by giving the actual formula used, this method of presenting the data is logical and, if carefully considered, reveals practically the same information as could be secured from a study of the results in connection with the formula itself.

Although I do not believe that the use of this method of presenting data should be encouraged—where possible authors should give complete data if their papers are to be of the highest value—I do believe that in case the formulas cannot be given, some method such as the one employed should be devised. Data presented in this manner does not lend itself readily to criticism. However, there are a few points of interest which should be emphasized.

1. The points of the highest acid resistance and the greatest toughness are not coincident in the case of the enamel used. In other words, if great toughness is desired, it is necessary to terminate the fritting just before the point of the highest acid resistance is reached. On the other hand, it is necessary to continue the fritting beyond the point of greatest toughness if high acid resistance is desired. My experience with a number of enamel formulas has confirmed this.

2. The remarkable decrease in B_2O_3 accompanying the increase in SiO_2 appears unusual. To my mind, it is doubtful whether the B_2O_3 volatilizes to the extent indicated under the short heat

treatment. I have found that, in making the chemical analyses of enamels, the B_2O_3 and SiO_2 are separated with difficulty and, unless great care is exercised, some of the B_2O_3 may be included with and reported as SiO_2.

It would add very materially to our knowledge if a reliable method for the chemical analysis of enamels containing fluorides, boric acid, Sb_2O_3, SnO_2, etc., were available.

3. I believe that the influence of the coefficient of expansion as a factor in shivering or crazing is greatly overestimated by enamelers. Fish-scaling is the *bête noir* of the enameling industry—especially of the sheet iron enameling branch. This phenomenon is presumably parallel to that of the shivering of glazes. It is evidenced by the scaling off of small flakes of the enamel and a resultant pitted surface—the steel being exposed in many places. It is supposed to be influenced largely by the coefficient of expansion of the enamel but in a recent set of experiments—involving the use of 120 ground coats of widely different chemical composition and applied to light steel—not one piece showed any fish-scaling when the enamel coating was properly applied and fired. But when improperly ground, applied or burned, or when applied on very heavy steel, fish-scaling was very prevalent. These facts, together with similar experiences in the past, lead me to believe that the mechanical manipulation of the enamel is a far greater factor in controlling fish-scaling than is the chemical composition.

R. R. DANIELSON: The authors of this paper present some interesting facts to the enameler—in that they very forcibly bring out the effects of undersmelting and oversmelting upon the enamel batch. Their conclusion that "variations in the properties of the enamel may be due to the volatilization of certain constituents in the batch" is instructive and may account for the irregularities which occur in the working of enamels—in spite of all the precautions taken in the processes of preparation and application.

Some of the irregularities in the data of this paper may be due to the method of sampling employed. It is quite possible that, in selecting a sample of undersmelted enamel, there might

be certain unfused refractory constituents, such as flint, etc., which would not pulverize as quickly as some of the other substances in the ball mill and which might fuse together to form a soft glass. In screening the sample through a 200-mesh sieve—unless the grinding had been very thorough—the coarser materials might be left on the sieve and consequently be eliminated from the frit. This would be especially true of the undersmelted enamels—since there would not be the homogeneity necessary in properly smelted enamels unless the entire sample were ground very finely and then quartered for the tests. This objection would also apply to the tests for acid resistance as carried out by the authors.

The authors have started a work which should be continued, for it will undoubtedly help to solve some of the problems encountered in enameling.

H. F. STALEY: The losses by volatilization, over and above those ordinarily assumed, are certainly high compared to those encountered in smelting enamels for cast iron. At the point "Y," at which the authors state this enamel would normally be poured, the loss, assuming the SiO_2 content to be constant from A on, is 11.8 per cent. From a series of carefully kept records extending over a period of years, I found that the loss in the smelting of cast iron enamels exceeded the theoretical loss by 1.9 to 3.0 per cent. and that part of this loss could be attributed to mechanical loss in the filling and emptying of the smelter. The difference must be largely due to the difference in composition of the two types of enamels. In the ordinary enamel for cast iron, used in this country, the B_2O_3 content varies from 6 to 12 per cent. The enamel used by the authors evidently contained a larger quantity of B_2O_3 for at "F" (Table 2) the loss by volatilization was 9.5 per cent., a considerable portion remaining in the fritted enamel.

It is noteworthy that the B_2O_3 and the bases were volatilized in approximately equal molecular amounts. This is in accord with results obtained by myself when working with borate glasses.[1] In these glasses, when the molecular ratio of base to B_2O_3 equaled

[1] "The Viscosity of Molten Glasses," Eighth Intern. Congr. Appl. Chem.

or exceeded 1 : 4, the ratio of the most acid pyrogenetic borate, there was no loss of B_2O_3 without loss of the base in the ratio existing in the melt. When the ratio of base to B_2O_3 was lower than 1 : 4, there was a corresponding loss of B_2O_3.

E. P. POSTE: Mr. Shaw's first point is very well taken and as a general conclusion has been confirmed a number of times. He is slightly in error, however, in his reference to the maximum acid resistance of this enamel. It is shown in Fig. 4 that the acid resistance at F is relatively high but that it has apparently not reached a maximum. In other words, had the smelting been continued a further increase in acid resistance would have resulted.

Our experience in the analysis of the boro-silicates does not confirm that of Mr. Shaw. Our B_2O_3 determinations were made on separate samples, the silica being determined in the usual manner. Fluorine was not found present. We were aware of the possible errors arising in the determination of B_2O_3 and Al_2O_3 and observed the necessary precautions as noted in Mellor's "Treatise on Ceramic Industries," Vol. 1, pages 584 and 589. Had any appreciable error of this nature occurred—the analyses would have totaled materially over 100 per cent. This was not found to be the case.

The remarks relative to the effect of the coefficient of expansion as a factor in fish-scaling are very interesting. Our recent observations have caused us to lose faith in the coefficient of expansion theory for fish-scaling—at least when the coefficient of expansion is alone considered and computed in accordance with the factors given in the Jena researches. We have come to the conclusion that, although this may be one of the factors, there are certainly other more important ones and principally those of elasticity and tenacity as has been so clearly pointed out by Staley.[1]

The criticism of Mr. Danielson is very pertinent—in so far as it applies to the method in general. It would perhaps be preferable to grind the entire sample so that it would pass a given mesh sieve rather than to take only that portion which had passed through the sieve. It is doubtful, however, whether the errors

[1] *Trans. Am. Ceram. Soc.*, **14**, 523–531 (1912).

resulting from this source could have materially affected the results in this case for it has been our observation that the amount of material retained on a 200-mesh sieve under the particular conditions of grinding was very small. The point is well worth keeping in mind, however.

The figures given by Mr. Staley—relative to the loss on smelting and in excess of the theoretical amount—would indicate a material difference in the types of enamels under consideration. Certain commercial formulas, in use at the present time, show a loss of from 3.0 to 5.0 per cent. in excess of the theoretical amount which we had formerly accounted for in the same way that Mr. Staley accounts for his losses of from 1.9 to 3.0 per cent. We conclude that some of this loss was due to volatilization. The enamel used in our experimental work was considerably softer than the ones concerning which commercial smelting data is available. No doubt the difference in the constitution of the enamels accounts for the apparent differences in the amount of material volatilized.

A COBALT-URANIUM GREEN GLAZE FOR TERRA COTTA.

By Hewitt Wilson, Columbus, Ohio.

We were confronted with the problem of developing a commercial green glaze having a deeper shade than any of the yellow-greens we had produced by the use of chromium stains in glazes fired to cones 6 or 7.

The characteristics and methods of producing green colors in glazes may be outlined as follows:

1. Copper greens are used extensively. At cones 6 or 7, however, the greater part of the copper is volatilized and the resultant shades of green are light and uneven.

2. Chromium and chromium stains when used in most glazes of the Bristol type give greens which appear yellow when compared with deep greens. The chromium can only be used in glazes in which the zinc content is very low. A reduction of the zinc content necessitates either a higher maturing temperature for the glaze or the use of lead compounds or frits. Chromium compounds are unstable in the kiln. In the proximity of even small amounts of chromium, glazes containing zinc oxide fade to brown and glazes containing tin are apt to be streaked with pink.

3. The nickel green colors are variable.

4. Iron compounds, if used alone, are volatilized at cones 6 or 7.

5. Uranium compounds, if used alone, produce variable yellow-green colors.

6. Greens may be produced by the blending of blue and yellow colors.

(*a*) It is reported that mixtures of iron and cobalt compounds have produced good greens. This has not been our experience—our trials giving browns and brown-greens.

(*b*) Orton notes the preparation, by roofing-tile manufacturers, of a green sulphate from antimony and cobalt oxides. Various yellow stains—some of which derived their yellow color from

antimony—were blended with cobalt and produced yellow and greenish browns which shaded into blues.

(*c*) Mixtures of cobalt oxide and titanium compounds are reported to have produced greens.

(*d*) Several investigators[1] have produced greens from mixtures of soluble uranium and cobalt compounds which were added to the glaze as insoluble frits.

In our attempt to develop the shade of green desired the procedure was as follows:

Series A.

Using a dull matt glaze as a base, uranium oxide and a cobalt stain were added to this glaze in varying amounts.

The formula of the glaze was as follows:

$$\left.\begin{matrix} 0.261\ K_2O \\ 0.306\ CaO \\ 0.294\ ZnO \\ 0.083\ BaO \\ 0.057\ MgO \end{matrix}\right\} 0.384\ Al_2O_3 \quad 2.08\ SiO_2$$

This glaze matures at from cones 3 to 7 in a commercial kiln. The blue stain added to the glaze had the following composition:

	Per cent. (Raw).
Cobalt oxide	16.0
English ball clay	53.0
Zinc oxide	31.0
	100.0

The commercial uranium oxide was supplied by the Carnotite Reduction Co. of Chicago. A rectangular series of 45 members was prepared by the addition of the cobalt stain and uranium oxide to the matt glaze. The corner glazes of the series were as follows:

Glaze No. 1—Matt glaze + 7.0% uranium oxide + 0.0% blue stain
Glaze No. 9—Matt glaze + 7.0% uranium oxide + 6.0% blue stain
Glaze No. 37—Matt glaze + 3.0% uranium oxide + 0.0% blue stain
Glaze No. 45—Matt glaze + 3.0% uranium oxide + 6.0% blue stain

[1] F. H. Riddle, *Trans. Am. Ceram. Soc.*, **8**, 210 (1906); R. H. Minton, *Ibid.*, **9**, 777 (1907); B. S. Radcliffe, *Ibid.*, **16**, 209 (1914); *La Céramique*, **1907**, No. 225, S. 25; *Tonind. Ztg.*, **1907**, S. 1412.

Each glaze was sprayed upon 3″ × 5″ terra cotta tile to which a coating of white underslip had been first applied.

The glazed tiles were placed in a commercial terra cotta muffle kiln and burned to between cones 6 and 7. The burning period was 70 hours and the cooling period 80 hours.

The appearance of the glazes of this series is noted as follows:

Glazes Nos. 1, 10, 19, 28, and 37, containing no cobalt stain, developed the characteristic uranium colors. 3.0 per cent. of

the stain produced a brownish yellow color, changing to green as the uranium content increased. The glaze containing 7.0 per cent. uranium oxide, although green, had a decided yellow cast.

Glazes Nos. 2, 11, 20, 29 and 38 were of deeper green shades and showed the influence of the stain but slightly.

Glazes Nos. 3, 12 and 21 were as green as any of the glazes of the series, but were not uniform when applied on large surfaces.

Glazes Nos. 30 and 39 were mottled by patches of yellow.

Glazes Nos. 4 to 9, 13 to 18, and 22 and 23 were uniformly deep green in color.

Glazes Nos. 24 to 27 developed a distinct blue-green color. The green color faded and the blue became stronger with increasing amounts of the cobalt stain.

Glaze No. 40 contained the smallest amount of the cobalt stain to show blue tints. When the uranium addition was lowest (3.0 per cent.), the blue shades were obtained with the lowest amounts of blue stain.

The glazes listed above as good deep greens were somewhat defective on account of the occurrence of yellow patches on the surfaces. There was no regularity in the occurrence of this yellow surface mottling. This mottling was very prominent in several of the good green glazes which were applied to full sized pieces of terra cotta. The appearance of the mottling was not very objectionable—in fact was pleasing—although not desired.

Series B.

Using a bright glaze of the following formula as a base, another series was prepared by the addition of the uranium oxide and cobalt stain in the same proportions as in Series A:

Bright Glaze:

$$\left.\begin{matrix} 0.238\ K_2O \\ 0.354\ CaO \\ 0.210\ ZnO \\ 0.144\ BaO \\ 0.055\ MgO \end{matrix}\right\} 0.428\ Al_2O_3 \qquad 2.90\ SiO_2$$

This glaze matures at from cones 4 to 7 when fired either in a small or large kiln.

The appearance of the glazes of Series B is noted as follows:

The colors developed were in general the same as those of the Series A glazes, although not as distinct. The green colors tend toward the brown and drab shades. The blue and yellow colors are less pronounced. The addition of uranium oxide alone tends to produce fine dark specks.

The yellow mottling developed by some of the glazes of Series A was not observed in any of the glazes of Series B. The mottling of the glazes of Series A may be explained as follows:

Since the uranium compound is partially soluble, a greater proportion of the yellow material was deposited near the surface of the glaze as the water evaporated in drying. The yellow color of the uranium partly masked the blue color of the insoluble stain and produced the mottled effect. Although the uranium does not come to the surface as a scum, it tends to take possession of the surface and the upper portion of the glaze—leaving a greater proportion of the blue stain next to the underslip. Any particles of blue stain which do appear on the surface are coated with sufficient uranium to appear green. Under the microscope, a cross section of the glaze coating shows that in places where the yellow-green does extend into the mass of the glaze a darker and bluer green results close to the underslip. As the bright glaze used in Series B produced no mottling, we may assume that it had greater solvent power than the matt glaze used in Series A.

Series C.

From the information secured from Series A and B a third series was prepared as follows:

In order to avoid the mottling of the matt glaze, a soluble blue stain was employed—the cobalt being added as soluble cobalt sulphate. Maintaining the uranium content constant at 6.0 per cent., the cobalt sulphate was added to the matt glaze (Series A) in varying amounts. The addition of 3.0 per cent. gave a reliable color, the proportion of uranium to cobalt sulphate in this case being 2 : 1. The matt glazes to which the cobalt sulphate was added were more vitreous than those in which the insoluble cobalt stain was used.

No signs of mottling were in evidence in the glazes of series C and the 3.0 per cent. cobalt sulphate glaze was used in the coating of 200 sq. ft. of terra cotta surface. A green glaze of this description can be burned in proximity to other glazes without danger of discoloring them.

By calcining or fritting the cobalt and uranium to a homo-

geneous mixture and by subsequent fine grinding a similar green can no doubt be obtained.

COMMUNICATED DISCUSSION.

R. L. CLARE: 1. I wish to state that whenever possible we have avoided the use of uranium compounds in terra cotta glazes on account of their excessive cost and we have usually been able to produce the various shades of green desired without the use of these materials.

2. We have used chromium alone in glazes and have found it to be very unstable and unsatisfactory. It, however, in some cases gives a very deep green color, deeper and better in fact than any which we have been able to secure by the use of a stain. It appears that the materials used in a stain with the chromium tend to dilute the green shade. Materials such as iron, cobalt or uranium when used in a stain change the shade to a brown-green, blue-green or a yellow-green.

3. It is very interesting to note that Mr. Wilson has produced a good green by the use of a mixture of uranium oxide and a cobalt stain. It is not clear in my mind whether his resultant green is of the same shade as the typical chromium green. We have produced greens by the use of mixtures of iron and cobalt stains and manganese and cobalt stains, but in each case they have developed yellow-green, blue-green or brown-green colors and in no case were the typical deep grass-greens of the chromium produced.

Mr. Wilson's theory of the cause of the mottling on the glaze surface is very interesting and plausible. We have often noticed scumming on the surfaces of some of our colored glazes and we have attributed it to the solubility of some of the colorants and the consequent concentration of salts on the surfaces of the pieces—due to evaporation. It has already been shown that colors can be produced by painting or spraying certain soluble salts in solution on the surfaces of the unburned terra cotta glazes.

D. F. ALBERY: I wish to note the following in reference to the methods of producing green colors in terra cotta glazes:

1. Copper oxide is satisfactory in glazes fired from approximately cone 04 to cone 2.

2. Chromium alone is too unstable to be recommended for the production of the green colors.

3. Chromium stains when properly compounded, calcined and washed, produce very stable and uniform greens of practically any desired shade. These green shades may be varied from deep blue-greens to brown-greens by the addition of cobalt oxide, iron oxide or burnt umber. The composition of the stain influences its color and shade considerably. For instance, it is possible to vary the shade of a given glaze by substituting plaster of paris for whiting in the stain. The composition of the glaze also has a decided influence on the stability of the color produced by a given stain.

We have made name panels by using a green glaze for the background and a white glaze—containing about 6 per cent. tin oxide—for the raised letters. The white glaze did not show the slightest discoloration even though it was in contact with the green glaze in a line at the base of the letters. It is largely a matter of glaze composition. Our green glazes are not fritted and do not contain zinc or lead.

4. I have never known of an iron compound producing a green color when used alone in a glaze at any temperature.

5. I have produced an unstable yellow-green by the introduction of a high percentage of uranium.

6. I have produced good blue-greens with cobalt-rutile combinations in glazes maturing at from cone 03 to cone 2.

Although good green colors may be obtained by cobalt-uranium combinations, it would appear that the cost of the high percentage of uranium oxide necessary would discourage the extensive use of this method.

R. H. MINTON: Those who have had experience in the manufacture of architectural terra cotta will appreciate the value of a dependable green coloring agent which is not affected by zinc oxide, and which will not affect, or be affected by, other colors. White, greens, browns and tans are widely used in polychrome work and a combination of these colors has always presented difficulties if the green was produced by the use of chromium compounds—the usual practice. Terra cotta white matt glazes

usually contain a high percentage of zinc oxide and, if used next to a chromium green, an unsightly line of tan or brown results at the juncture. For this reason, a green produced from a mixture of uranium and cobalt greatly simplifies the factory operation.

My experience with the use of uranium compounds for yellows and greens has covered its use in both fritted and raw, bright and matt glazes, and has shown that in order to produce a good yellow from uranium in a matt glaze, the zinc oxide should be eliminated as it tends to the development of greens. I have found that in order to produce uniform uranium colors, either yellow, orange or green in a matt glaze, it is of great advantage to use a small amount of rutile. The rutile appears to "set" the color and prevent the irregularity of color so often produced by uranium. An excellent green may be produced by the use of cobalt and rutile with the addition of a small amount of oxide of iron, although the color is not quite so bright as that secured with the presence of some uranium.

The mottling of the color in the matt glaze is undoubtedly due to the failure of the glaze to dissolve the uranium and the consequent crystallization or segregation, upon cooling. This difficulty is almost always encountered in producing uranium yellow matt glazes, where reducing conditions may occur, the result being a mottled green-yellow. The addition of rutile will entirely overcome this defect and the color will be improved if the content of zinc oxide is kept very low. A high zinc content and reducing atmosphere in the kiln are favorable for the production of greens. The use of the soluble form of the cobalt, rather than the difficultly soluble stain, as stated by Mr. Wilson, probably caused the formation of the green color by solution of the cobalt and uranium instead of by suspension.

HEWITT WILSON: The uranium-cobalt greens developed in the above study are not of the same shade as the typical chromium greens. The color is a deeper green than that afforded by the majority of the chromium greens burned in terra cotta muffle kilns to cone 6. While it is true that the cobalt-uranium greens do not match the characteristic chromium greens, it is likewise

true that it would be difficult to match some truly acceptable uranium-cobalt green shades with chromium combinations.

There is no question as to the practicability of producing green colors from cobalt and uranium mixtures. They have been produced in regular terra cotta work in a quantity sufficient to insure the uniformity required.

The disadvantages of the high cost of uranium is not so great when the comparatively small amount of green glazed terra cotta produced is considered. We do not know of any single component for colored glazes which has caused more terra cotta trouble than chromium.

The advantages of the above uranium oxide–cobalt sulphate green are as follows:

1. Ease of preparation. No calcining, washing or extra grinding necessary.

2. So far as noted, there was almost no discoloration of adjoining glazes—regardless of their composition.

3. A greater range of glaze composition in which green colors can be produced. It can be used in zinc and tin glazes.

Although it is not claimed that uranium-cobalt greens will replace the chromium greens, they have a place in terra cotta work in which uranium shades are desired and the complexities of chromium troubles are to be avoided.

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ALABASTER GLASS: HISTORY AND COMPOSITION.

By Alexander Silverman, Pittsburgh, Pa.

Alabaster is a term usually applied to semi-opaque glasses which transmit the light from a source, diffusing it, but not materially altering its color. The name was probably applied because of the close resemblance which these glasses bear to natural alabaster. The French use the term "Albatre" or "Pate de Riz" (rice paste). Opal glasses are also semi-opaque but the light transmitted acquires an opal or fiery color.

During researches by the writer on the production of alabaster and opal effects considerable historical material has been gathered and is presented here for ceramists who may be interested.

In the museum exhibits one frequently encounters collections of Chinese snuff bottles which are made of alabaster glass. Some of these,[1] coming from the Ch'ien Lung dynasty (1736–1795), are almost 200 years old. According to one authority, alabaster glass was made in Venice and Murano at about 1600. Some early Egyptian glasses show slight alabaster effects which are probably due to imperfect melting or to devitrification during the ages in which they lay buried.

"Manuel Complet de Verrier," by M. Julia de Fontenelle, published in Paris in 1829, mentions alabaster glass on page 30.

H. Leng[2] speaks of the use of lead sulphate in the manufacture of opal glass. The writer's experience, certain details of which will be given later, points to alabaster formation in the presence of sulphates, so it is possible that Leng's opal was alabaster.

Deming Jarvis[3] gives the following formula for alabaster glass: "500 lbs. batch (probably crystal glass), 30 lbs. phosphate of soda, 10 lbs. allumine (calcined alum), 3 lbs. calcined magnesium." On page 116, Jarvis states that alum loses 60 per cent. on cal-

[1] Carnegie Museum, Pittsburgh, Pa.

[2] "Handbuch der Glasfabrikation," 1854.

[3] "Reminiscences of Glass Making," New York, 1865, p. 106.

cining. Assuming its conversion to Al_2O_3 and K_2SO_4, it should lose 70.8 per cent., and it is therefore probable that the material was either partly decomposed potash alum or some other substance called alum in that day.

Hoch[1] mentions alabaster as one of the oldest known glasses and states that melasse (beet sugar potash bearing sulphates and chlorides) was employed.

Raimund Gerner[2] mentions the use of salt in the preparation of cloudy glass and gives the following formulas:

1.	Parts.	2.	Parts.
Sand	100.0	Sand	100.0
Slaked lime	2.0	Slaked lime	13.0
Bone ash	5.5	Tin oxide	1.0
Potash	44.0	Potash	38.0
Salt	5.5	Salt	1.5
Arsenious oxide	0.7	Arsenious oxide	0.25
Cullet	50.0	Borax	1.0

It is unlikely that the alabaster effect was produced by the salt alone. The bone ash probably functioned in batch 1 and the tin oxide in batch 2, and the arsenious oxide in both.

Before the extensive working of the Stassfurt mines in Germany, much of the potash was derived from plant ashes and large quantities were imported from Russia. This material contained considerable quantities of sulphates and chlorides which were partly conducive to the production of the alabaster effect.

In the second edition of Gerner's book, Leipzig, 1897, page 211, is given the following batch:

	Parts.		Parts.
Sand	50	Cryolite	7
Soda	8	Litharge	2
Alumina (Alaunerde)	4	Lime	3
		Saltpetre	2

On page 34 of the same publication he states that "potash, until very recently, was prepared from wood and plant ashes. Beech ashes (Buchenholzasche) contain K_2CO_3 15 per cent.,

[1] *Dingler's polytech J.*, **224**, 623 (1877).

[2] "Die Glasfabrikation," Vienna, **1880**, p. 267.

Na_2CO_3 3 per cent., K_2SO_4 2 per cent., and the remainder water-insoluble matter." On page 35 he states that "Refined beet potash contains K_2CO_3 92 per cent., Na_2CO_3 5 per cent., KCl 3 per cent., also K_2SO_4." On page 36 he gives the following analyses of potashes:

	K_2CO_3.	Na_2CO_3.	K_2SO_4.	KCl.
American potash	71	8	16	3
Illyrian potash	89	0	1	9
Russian potash	69	3	14	2
Wool Sweat (Suint)	72	4	6	6
Refined Beet Ashes (Melasse)	90	2	3	3
Stassfurt	97	0	1	1

On page 59 he dwells upon the use of spars and alumina and on page 212 states that "alumina may be substituted for the cryolite, feldspars, etc."

Gessner[1] refers to the use of alumina in quantities of from 7 to 20 per cent.

Furnival[2] states that American pearlash contains about 7 per cent. K_2SO_4.

Hans Schnurpfeil[3] also calls attention to the presence of sulphates and chlorides in potash.

Fontenelle and Malepeyre[4] state that equal parts of chalk and Al_2O_3 when melted together yield a glass resembling pearls, and give a formula for the preparation of a white, translucent glass, as follows: Sand 100, chalk 32, Al_2O_3 68. In vol. II, p. 242, they discuss the manufacture of alabaster glass in Bohemia.

Paul Randau[5] gives the following alabaster batch containing sulphates:

100 parts	Feldspar	35 to 71 parts
	Fluorspar	17 to 50 "
	Barytes	12 to 40 "
melted with	Soda	15 to 50 "
	or Potash	20 to 65 "
	and Sand	70 to 120 "

[1] *Glassmakers Handbook*, Pittsburgh, **1891**, p. 148.
[2] "Researches on Leadless Glazes," **1898**, p. 54.
[3] "Schmelzung der Glaser," **1906**, p. 11.
[4] "Manuel du Verrier," Paris, **1**, 59 (1900).
[5] "Die Farbigen, Bunten and Verzierten Glaser," Vienna, **1905**, p. 106.

These proportions are also given in a patent[1] granted to J. Kemper.

An article by Richard Zsigmondy[2] on "Cryolite and its Substitutes," mentions the use of china clay and sodium fluoride in alabaster batches, stating that the best results are obtained by adding a quantity of china clay equivalent to the sodium fluoride in the cryolite.

The following formulas[3] are suggested for the use of alumina and sodium fluoride:

	Parts.	Parts.
Sand	100	100
Sodium fluoride	10	6
Alumina (Alaunerde)	14	10
Fluorspar	0	10
Feldspar	0	8

The use of sodium fluoride in alabaster glass is covered in a patent[4] issued to Adolf Tedesco, who gives the following formula:

	Parts.	
Sand	156	
Sodium fluoride	33	—(containing 10 per cent. sodium carbonate)
China clay	15	
Chalk	10	
Soda	5	

In this patent the inventor claims the use of sodium fluoride only, so that the use of alumina in alabaster batches must have been known to glass makers.

Weinreb[5] mentions the use of a mixture of SiO_2 100 parts, Na_2F_2 20 parts, K_2CO_3 8 parts, Na_2CO_3 7 parts, $CaCO_3$ 8 parts, and $Al_2(OH)_6$ 6 parts, which, he states, yielded a beautiful, white glass.

In the *Journal of the Society of Chemical Industry*[6] is noted a statement that "Since, however, fluorine (from cryolite) attacks the glass-pots and thus leads to contamination of the glass,

[1] D. R. P. 4551, July, 1878, *Dingler's polytech. J.*, **233,** 269 (1879).
[2] *Ibid.*, **271,** 40 (1889).
[3] *Sprechsaal,* **30,** 556 (1897).
[4] D. R. P., 31,112, November, 1883.
[5] *Dingler's polytech. J.*, **256,** 365 (1885).
[6] *J. Soc. Chem. Ind.*, **18,** 916 (1899).

feldspar or alumina is sometimes added, the composition of the mass being modified as follows: Sand 50 parts, potash 4 or 5 parts, soda ash 5 or 6 parts, cryolite 7 parts, feldspar or alumina 5 parts, lime 5 parts, and nitre 3 parts. A cheap substitute for cryolite is fluorspar which, however, has to be neutralized by alumina in order to prevent corrosion of the pots, etc. A typical mass is prepared from a mixture of sand 50 parts, soda ash 8 to 10 parts, potash 3 to 4 parts, fluorspar 10 parts, alumina 5 to 10 parts, nitre 2 to 3 parts, zinc white 2 to 3 parts, feldspar 0 to 10 parts, etc. A mixture of sodium fluoride and alumina is also cheaper than cryolite, etc. The mass is compounded from a mixture of sand 50 parts, potash 6 parts, soda ash 6 parts, sodium fluoride 4 to 6 parts, alumina 5 to 8 parts, feldspar 6 parts, nitre 1 part, minimum 3 parts, or zinc white 2 parts, and lime 0 to 3 parts."

The references cited in the preceding paragraphs show clearly that the use of mixtures of alumina, sulphates and chlorides with other raw materials is not original with American chemists and manufacturers although they have produced some of the finest alabaster glasses of superior quality and commercial value. No explanation of the cause of the alabaster effects is offered by the early writers except that of devitrification. The author believes that sulphates and chlorides serve as ionized electrolytes in the hot liquid, precipitating various colloidal suspensions which would otherwise cause opalescence.[1]

In the writer's researches on alabaster glass a number of interesting facts have been developed. Fluorides with alumina or aluminium bearing substances produce opalescence until sufficient quantities of sulphates or chlorides are introduced when the opacifying materials gather in larger particles and white light is transmitted. The bivalent ion of the sulphates produces more intense whiteness than the monovalent chloride. This is in keeping with the behavior of electrolytes towards aqueous colloidal suspensions.

The presence of barium[2] compounds enhances the white color—

[1] A. Silverman, "Similarity of Vitreous and Aqueous Solutions," *J. Ind. Eng. Chem.*, **9**, 33 (1917).

[2] A. Silverman, "The Use of Barium Compounds in Glass," *J. Soc. Chem. Ind.*, **34**, 399 (1915).

probably through the formation of barium fluosilicate. Cryolite produces increasing whiteness up to a certain concentration. The color then gradually loses intensity with the introduction of larger quantities and finally disappears. This effect resembles the solution of precipitates in aqueous solutions in the presence of an excess of the precipitant.

Alumina and the chlorides were employed in the writer's researches prior to 1904 and sulphates were introduced in 1912. As the result of these researches a commercially successful alabaster glass[1] of American manufacture was placed on the market. The limited solubility of the chlorides and sulphates in the silicates led to a considerable reduction of the quantities introduced into the batch, with an accompanying increase in the life of the pots which are attacked by fused chlorides and sulphates.

When the alumina was replaced by its equivalent of feldspar, a beautiful, speckless glass of much higher than normal viscosity resulted. Magnesium silicate also produced the alabaster effect. The following formulas for American alabaster glasses are contained in patents:[2]

	Parts.		Parts.
Sand	100	Sand	345.8
Lead oxide	$15^5/_8$	Litharge	56.8
Soda	$21^7/_8$	Soda ash	86.4
Niter	$5^1/_2$	Cryolite	20.0
Salt	$5^1/_2$	Aluminium oxide	60.0
Borax	$1^1/_4$ to $2^1/_2$	Niter	32.0
Aluminium hydroxide	18.12	Borax	8.0
Fluorspar	6	Plaster of paris	5.0

	Parts.
Sand	100
Soda ash	49
Red lead	56
Feldspar	120
Sodium fluoride	$7^1/_2$
Strontium sulphate	$1^3/_4$
Sodium chloride	5
Alumina	$22^1/_2$
Niter	5
Antimonious oxide	$^1/_2$

[1] A. Silverman, "The Chemist and the Glass Manufacturer," *Trans. Am. Ceram. Soc.*, **12**, 187 (1910).

[2] U. S. Patents 1,097,600–1,143,788 and 1,245,487.

Although the most desirable alabaster glasses are produced by aluminium-bearing substances with fluorides and chlorides or sulphates, this article would not approximate completeness without mention of other types given in the literature. Calcium phosphate, magnesium silicate, stannic oxide, arsenious oxide, zirconium oxide[1] and titanium oxide[2] are also employed. Analyses of some alumina-bearing alabaster glasses have revealed the presence of considerable quantities of zirconia, presumably introduced as an impurity in the alumina.

Alabaster effects may also be obtained in high silica glasses through devitrification. Raimund Gerner[3] suggests the following batches:

	1.	2.	3.	4.	
Sand	200	200	250	100	parts
Pearlash	80	70	100	42	"
Bone ash	12	10	15	..	"
Magnesium silicate	9	3	14	8	"
Arsenious oxide	1	1	..	..	"
Saltpetre	..	10	15	5	"

Wilhelm Mertens suggests:[4]

	1.	2.	3.	
Sand	75	75	100	parts
Pearlash	28	30	38	"
Bone ash	7	7	..	"
Saltpetre	6	8	4	"
Magnesium silicate	..	10	10	"
Red lead	..	..	12	"
Arsenious oxide	1	0.5	..	"

Randau[5] gives this batch: Sand 100 parts, calcium carbonate 40 parts, talc 5 parts and borax 5 parts.

Rudolf Hohlbaum[6] suggests:

[1] D. R. P., 189,134.
[2] D. R. P., 18,708.
[3] "Die Glasfabrikation," p. 206.
[4] "Die Fabrikation und Raffinierung des Glases," p. 214.
[5] "Die Farbigen, Bunten und Verzierten Glaser," 1905, p. 112.
[6] "Herstellung, Bearbeitung und Verzierung des Feineren Hohlglases," 1910, p. 135.

	1.		2.		3.
Sand	100 kg.		100 kg.		100 kg.
Pearlash (65%)	41 kg.	(80 to 85%)	45 kg.	(60 to 65%)	40 kg.
Calcite	...		17 kg.		...
Bone ash	...		11 kg.	Guano	7 kg.
Magnesium silicate	10 kg.		...		2 kg.
Saltpetre	...		...		3 kg.
Manganese dioxide	200 g.		200 g.		200 g.

	4.
Sand	100 parts
Pearl ash (60 to 65%)	39 "
Red lead	30 "
Boric acid	7 "
Saltpetre	4 "
Bone ash	2 "
Stannic oxide	2 "

Additional formulas are mentioned in other books and in journals. Most of these batches fail to work in American factories. They are usually intended for low temperature slow melting furnaces. In some foreign factories the glass is ladled into water and then remelted.

It may now prove of interest to consider the break of continuity in the history of alabaster glass caused by the introduction of opal glass. The earlier white glasses were chiefly alabaster, due, as has already been intimated, to the effect of chlorides and sul-

phates, present as impurities in the various types of potash, and causing the precipitation of the colloids in the glass. When the purer refined pearl ash, prepared from Stassfurt salts and sugar beet waste, became available the absence of powerful electrolytes, or the presence of only very small quantities of electrolytes, prevented precipitation and the smoother opal glasses came into general use. During the latter decades of the nineteenth century opal glass displaced albaster to a great extent. When American manufacturers succeeded in preparing it on a commercial scale in the early part of the present century they felt that they had made a discovery. What they really had done was to introduce the chloride or sulphate, missing in the pure pearl ash, and so necessary for precipitation. In other words, they obtained through the application of scientific principles a result which impurities in their raw materials had accidentally given to the foreign manufacturers.

The writer conducted an extensive correspondence with glass makers in England, France, Belgium, Italy, Germany and Austria during 1913 in order to secure definite historical data in reference to alabaster glass. The diversity of opinion which follows shows how difficult it is to settle such questions. The date indicates the year in which the manufacture of alabaster glass began according to the informant whose name is given. Where the date is marked (S) a specimen was received which is in the writer's collection. (M) indicates that the informant manufactured alabaster glass. A photograph of some of these specimens is shown on the preceding page.

MANUFACTURERS OF ALABASTER GLASS.

1600	The Venice & Murano Co., Venice, Italy.
1700	Josef Janke & Co., Haida, Austria. (Manufactured by Chinese and Japanese.)
1810	Josef Knizek, Ullersdorf, Austria.
1810	E. Michel & Co., Teichstadt, Austria.
1810	Josef Rindskopf's Soehne, Teplitz-Schoenau, Austria.
1810	J. Schreiber & Neffen, Wien, Austria.
1820	Josef Janke & Co., Teichstadt, Austria. (1820 Haida, Bohemia. After 1840 in nearly all Bohemian huts. Made with Russian potash instead of ordinary potash. Many old specimens in Janke museum.)

1830 Josef Rindkopf's Soehne, Dux, Austria. (Made by father in Tischen, Austria, 1860.)
1840 M Wilhelm Kralik, Johann Mayer Factory, Winterberg, Austria.
S 1840 Compagnie des Cristallerie de Baccarat, Paris, France.
1840 M Meyer & Neffen, Winterberg, Austria.
1850 M Brueder Gerhart, Mulan and Podiebrad, Austria.
S 1850 Jilck & Vetter, Steinschoenau, Austria. Colored by bone ash, talc and magnesium silicate.
1850 M Carl Goldberg, Haida, Austria. Has piece manufactured by father in 1850.
1850 M Arthur Rudd & Co., Lancashire, England. (Also made at Birmingham, Stourbridge and London.)
1850 M Molineux Webb & Co., Ltd., Manchester, England. (Trade name "Carnelian.")
S 1860 M E. Michel & Co., Teichstatt, Austria.
S 1863 Herman Heye, Hamburg, Germany. (Bowl in illustration.)
S 1864 M Bartles, Tate & Co., Manchester, England. (Trade mark "Cornelian.")
S 1860 M Raimund Knospel and Soehne, Hillemuehl, Austria.
1860 M E. St. Clair (Crystallerie de Baccarat), London, England. (Trade Mark "Agate.")
1870 M J. Schreiber and Neffen, Gr. Ullersdorf, Austria.
S 1870 M Tietze and Seidensticker, Penzig, Germany.
1870 M Constantin Kopp, Klein-Anjezd, Austria.
1880 M August Walter Soehne, Moritzdorf, Germany. (Vases and illuminating ware.)
1880 M Josef Palme, Post Kitlitz, Austria.
1880 M Glashuetten-Werke Carlsfeld, Carlsfeld, Germany.
S 1884 M Anton Rueckel & Sons, Nischberg, Austria.
S 1888 M Joseph Knizek, Ullersdorf, Austria. (Small vase in illustration made by father. Batch: sand 150, potash 65, magnesium silicate 7, saltpetre 6, bone ash 8.)
1890 M Wilhelm Kralik Sohn, Eleonarehhain, Austria.
S 1892 M Val Saint Lambert Glassworks, Belgium. (Lamp fount in illustration.)
1898 M Glasindustrie Schreiber Aktiengesellschaft, Berlin, Germany.

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(See *Sprechsaal, Keram Rundschau, Glas-Industrie* and *Diamant*, complete sets of which were not available in Pittsburgh when this list was prepared.)

SCHOOL OF CHEMISTRY,
UNIVERSITY OF PITTSBURGH.

THE ZWERMANN TUNNEL KILN AND ITS OPERATION.

By Carl H. Zwermann, Kalamazoo, Mich.

It would appear that the following points are essential in the construction and operation of a successful tunnel kiln:

First, as the tunnel kiln, on account of its fuel and labor-saving qualities, is intended to replace the periodic kiln, it would appear that it must be so constructed and operated as to enable one to produce the same conditions as in a periodic kiln.

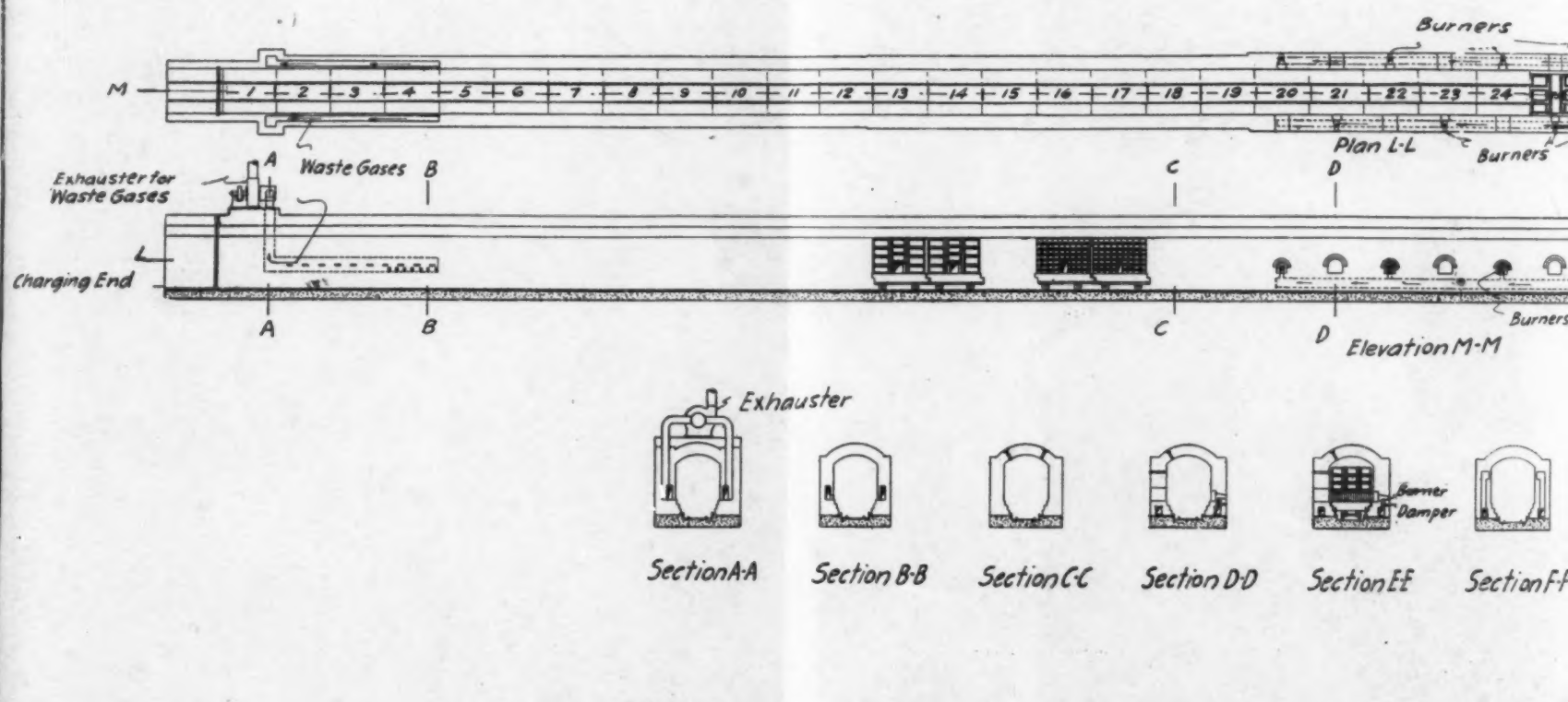
Second, the succees of a tunnel kiln depends more upon having it under good control than upon any other factor.

Third, as the first cost of a tunnel kiln is considerably higher than that of a number of periodic kilns of equal capacity, it should be so constructed as to have a comparatively wide tunnel. A tunnel kiln twelve feet wide costs comparatively little more than a tunnel kiln four feet wide, and has about three times the capacity—the heat loss through radiation being proportionately less.

Fourth, the design of the kiln should be as simple as possible so as to require the minimum of repairs. It must be so constructed as to reduce to a minimum the heat losses through radiation and so as to utilize the heat from the cooling zone for drying or heating purposes.

The Zwermann oil-fired kiln, illustrated in Fig. 1, is being operated at Kalamazoo. This kiln is about 352 feet long, including the vestibule, the tunnel being 6′ 4″ wide and 6′ 6″ high from the top of the trucks to the arch. It will hold 46 trucks, including the one in the vestibule, each truck being 7′ 7 1/2″ long. There are nineteen trucks in the preheating zone up to the first burner, eight trucks in the firing zone and eighteen trucks in the cooling zone.

The entrance to the kiln is through a vestibule provided with two tightly fitting rolling doors. A rolling door was originally provided at the outlet end of the kiln but this has been found unnecessary. A hydraulic pusher is installed at the entrance to


Burners
M
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
Plan L-L
Burners
Exhauster for Waste Gases
A
Waste Gases
B
C
D
L
Charging End
A
B
C
D
Burners
Elevation M-M
Exhauster
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Section B-B
Section C-C
Section D-D
Section E-E
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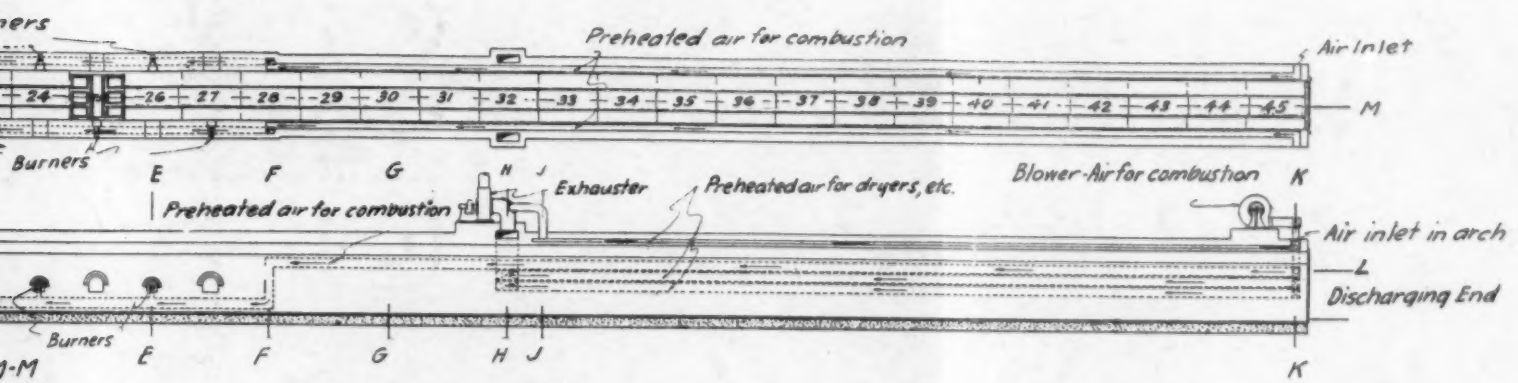

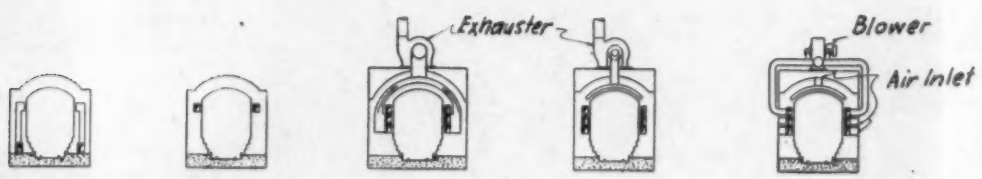

Section F-f Section G-G Section H-H Section J-J Section K-K

ZWERMANN'S TUNNEL KILN
(Patent Pending)

SK-726

the kiln, the pusher rod passing through an opening in the vestibule door, the entire train being advanced one truck length at a time. About three minutes are required to introduce and remove one truck. The loaded trucks are introduced at two-hour intervals, 92 hours being required to pass a truck through the kiln.

The kiln gases are drawn off by means of an exhaust fan near the entrance end. The waste gas outlets are at the fourth truck from the vestibule, on a level with the tops of the trucks, and lead through a flue in the sides of the kiln, extending as far as truck No. 1 and then out through the exhaust. Mechanical draft was preferred as it permits of closer control than stack draft. A second exhaust, located about midway in the length of the kiln, draws cold air through the hollow arch and side walls of the cooling zone of the kiln and passes it through the ware. This pre-heated air is utilized in the drying and pre-heating of the ware. The ware is indirectly cooled by this air, which does not pass through the tunnel or come into contact with the ware. The heat from the cooling ware in both kilns is sufficient to heat the factory and dryers during very severe weather.

The pressure blower, which delivers the air for combustion to the burners, is located on the outlet end of the kiln. This air is passed through recuperators built in the side walls of the cooling zone.

The trucks are of substantial steel construction with cast iron wheels and have a plate on either side which runs in a sand seal. Each truck is covered with a layer of insulating material, on top of which is placed a layer of fire brick tiles. The ware is stacked around and above a combustion chamber which is built on the center of each truck. This combustion chamber is at right angles to the tunnel.

The kiln walls are constructed from a layer of 9″ fire brick, $8\frac{1}{2}$″ of common brick and a variable thickness of kieselguhr. The arch is built of 9″ fire brick and is also insulated with kieselguhr. The insulation of a tunnel kiln is very necessary in order to reduce the heat losses through radiation. Temperature readings, taken at a point at which the internal temperature of

the kiln was 1430° F., gave 102° F. at the surface of the outer wall and 120° F. at the surface of the top of the arch. At another point, at which the internal temperature was 2300° F., the outside surface temperature was 135° F. and the surface temperature of the top of the arch was 142° F.

The ten oil burners used are located on both sides of the kiln. At the two last trucks in the firing zone the burners are opposite each other, the balance being located alternately on either side of the kiln. Eight trucks, in all, are opposite the burners. The location of the trucks in the kiln is so arranged that when at rest the center of each combustion chamber on a truck is opposite the center of a burner.

The oil is delivered to the burners under pressure and is atomized with compressed air. The balance of the air for combustion is supplied, pre-heated, by the pressure blower as already described. All of the air for combustion is blown through the burner blocks and excellent combustion is continually maintained in the combustion chamber. With the arrangement of the burners and air supply described, the kiln may be operated either with a reducing or oxidizing fire by a slight change of the dampers controlling the air supply. This is very necessary in the burning of certain classes of products. In a periodic kiln the atmosphere is somewhat reducing after every coaling and oxidizing after the fires have burned down. The same condition may be created in the Zwermann kiln with little or no difficulty.

The combustion chamber, being built on the truck proper, the making of repairs is simplified and the heat is delivered directly to the center and at the bottom of the material being burned. This, and the fact that the kiln is under excellent control, assures an even distribution of heat and a very uniform firing of the ware. Furthermore, the location of the combustion chambers on the trucks and transversely to the tunnel permits the building of a much wider kiln.

For wares burned in saggers, a combustion chamber on the top of each truck is required in order to permit of the ware being stacked. If bricks are being burned no special combustion cham-

ber structure is necessary—the brick being set so as to form their own combustion chamber.

The burners may be regulated at will and the desired temperature maintained at each one. Eight thermocouples are inserted through the arch in the heating zone of the kiln at Kalamazoo. These are connected to a recording galvanometer. By providing the necessary sight holes in the burning zone the burning may be regulated by means of cones—although better control is had by the use of pyrometers. The desired temperature is maintained for days and weeks without the pyrometer charts showing large variations. The temperature of the ware when it reaches the first burner is about 1000° F. After the temperature desired at each burner has been determined it can be maintained without great variation.

The waste gases leave the kiln at a temperature of about 300° F. Obviously, the percentage of excess air introduced into the kiln is controlled by the regulation of the exhaust.

The quantity of the ware loaded on the cars has been found to be an unimportant factor in the operation of this kiln. When the kiln was first started, there was not enough ware on hand and some empty trucks were passed through. Those following were loaded only to one-half of the height of the tunnel. In every instance, however, the ware was well burned, no overburned or under-burned pieces being noticed. This was probably due to the location of the combustion chambers at the top of the trucks as well as to the method of firing and regulating the kiln.

We have determined that if the pressure blower, supplying the outside air and also the preheated air from the cooling zone for combustion, was cut out, a large percentage of defective ware and uneven firing resulted. A difference of as high as two cones, between the top and bottom of the truck, was noticed. The highest temperature was at the bottom, although when the kiln was operated under proper control the greatest difference in temperature found between the top and bottom of a truck load was about one-half cone—the ware being burned to cone 9.

The first kiln erected at Kalamazoo is 352 feet long; the second kiln is 285 feet long. Although a longer kiln permits the for-

ward movement of the trucks at shorter intervals, the length of a kiln should obviously be dependent upon the capacity desired and the material to be burned.

Summary.

The experience gained during the period in which the Kalamazoo kiln has been operated demonstrates that, in order to produce marketable ware of any kind and particularly sanitary porcelain, an absolute and convenient control of the kiln is necessary in order that the human factor may be eliminated as far as possible.

It is our conviction that the Zwermann kiln may be used in place of the periodic kilns in the firing of many kinds of ceramic wares. The water-smoking and pre-heating zones are under better and more even control than in a periodic kiln. The cooling of the ware is done just as efficiently as in a periodic kiln. By the use of the tunnel kiln we have made a considerable saving in fuel over that required in the firing of the periodic kilns. A considerable saving in labor has also been noted. A skilled fireman is not required. As the trucks are loaded and unloaded in the open, this work is also lighter and easier and does not require the services of skilled kiln setters.

THE PROPERTIES OF SOME OHIO AND PENNSYLVANIA STONEWARE CLAYS.[1]

By H. G. Schurecht, Columbus, Ohio.

Introduction.

The resistance of vitrified clay to chemical action, together with its impenetrability to liquids, has made chemical stoneware an important product in the chemical industries. Stoneware distilling kettles, receivers, filters, condensing worms, centrifugal pumps, acid-proof pipe fittings, tower packing, acid-proof tanks, photographic tanks, and troughs and tubes for electrical purposes are used in these industries. Stoneware equipment is also used in the various food industries, including the sugar industry. Owing to the increased production of explosives during the war, there has been a marked increase in the demand for chemical stoneware and for stoneware clays. The wider use of chemical stoneware is only limited by its comparative brittleness and its sensitiveness to sudden temperature changes.

Composition and Properties of Chemical Stoneware.

The clays or bodies used in the manufacture of chemical stoneware should have good bonding power, a small drying and burning shrinkage, and a somewhat wide vitrification range. Crushed stoneware is sometimes added to reduce the shrinkage. Feldspar or a mixture of feldspar and a small percentage of calcium carbonate is sometimes added as a flux. Since the color of chemical stoneware is not an important consideration, cheaper fluxes, such as phonalite, trachyte, porphyry, and retinite, have been used in Europe[2] in place of feldspar. The chemical analysis of a variety of phonalite is as follows:

[1] By permission of the Director, Bureau of Mines.

[2] Kerl, B., Cramer, E., and Hecht, H., *Handbuch der gesammten Thonwaaren industrie*, Friedrich Vieweg und Sohn, Braunschweig, 1907, p. 1320.

SiO_2	50.09
Al_2O_3	23.96
Fe_2O_3	2.30
CaO	1.22
$CaSO_4$	1.41
MgO	0.28
K_2O	9.28
Na_2O	8.05
H_3PO_4	0.05
CO_2	0.22
H_2O	3.27
	100.13

These minerals are found in this country in Texas, South Dakota, Wyoming, Missouri, Minnesota, Utah, Arizona, and Colorado.[1] Albany slip is also sometimes used as a flux in chemical stoneware.

There are many different uses for chemical stoneware and hence the body must be varied to meet the different requirements. Corundum[2] is sometimes added to the body in case unusual resistance to temperature changes is necessary. In case the ware must be unusually resistant to chemical action—a high degree of vitrification is desirable. For certain purposes, the ware should be very resistant to shocks and strains and therefore the body should be unusually tough and strong when burned. The physical properties of the ware are as important as the chemical properties.

A salt or slip glaze is commonly used in the manufacture, although a glaze corresponding to the formula of cone 1 is sometimes employed for ware which is burned to cone 4. Carborundum,[3] because of its resistance to chemical action, is sometimes applied as a coating on chemical stoneware—water glass or boric acid being used as a binder.

[1] Clarke, E. W., "Analyses of Rocks," *U. S. Geol. Surv. Bull.*, **591**, 376 (914).

[2] D. R. P. Nr. 158,336.

[3] Kerl, B., Cramer, E., and Hecht, H., *Op. cit.*, p. 961.

The Occurrence of the Clays Investigated.[1]

Tionesta Clay, Ellis, Ohio.

A sample of Tionesta clay, from the drift mine of Joseph Moody, located one mile south of Ellis, Muskingum County, is designated as "A" in the text. This clay is shipped to the potteries at Zanesville and Cambridge, Ohio, and is used in the manufacture of art ware, mosaic tile, and cooking ware. The sample was taken from a stock pile of the clay. The vertical section of the mine is as follows:

	Ft.	In.
Shale	15	0
Limestone, Putnam Hill	4	9
Clay and shale	12	0
Sample "A" Clay, light, plastic, Tionesta	4	10

Lower Kittanning Clay, Roseville, Ohio.

The sample was taken from an open cut mine of the Hydraulic Press Brick Co., at Roseville, Muskingum County, and is designated as "B" in the text. This bed has a sufficient surface covering so as to be unaffected by weathering. A vertical section is as follows:

	Ft.	In.	
Shale	12	0	
Shale, dark	0	2	
Coal, rough	0	6	Middle Kittanning
Shale	0	3	
Coal	1	7	
Clay	0	1/2	
Coal	1	9	
Clay, siliceous	1	2	
Sandstone, irregular bedded	3	2	
Shale, gray	7	0	
Sandstone, shaly	3	6	
Shale, gray	6	4	
Coal, shaly	0	1	
Clay, plastic, dark gray	5	0	Oak Hill
Clay, plastic, with large nodules of ferruginous limestone	2	0	
Clay, plastic light	1	0	
Clay, flint, light gray	3	0	
Coal, smutty, lower Kittanning	0	1	
Sample "B" Clay, plastic, light to dark gray	6	8	

[1] The Ohio clays were sampled by Mr. Wilbur Stout of the Ohio Geol. Survey.

Lower Mercer Clay, White Cottage, Ohio.

The sample of Mercer Clay, designated "C," was taken at the open cut mine of W. F. Gerhart, located about one mile west of White Cottage, Muskingum County. This clay is used extensively by the Muskingum Pottery Co., White Cottage, and by the A. E. Hull Pottery Co., Crooksville. Although the bed is under shallow covering, the clay is but little weathered. A vertical section is as follows:

		Ft.	In.	
	Limestone, Lower Mercer	1	1	
	Shale	0	3	
	Coal, bony	0	2	Middle
	Coal, good	0	3	Mercer
	Clay, light, siliceous	2	10	
	Coal, shaly	0	3	
	Clay, siliceous, light, lower part ferruginous	5	0	
Sample "C"	Clay, dark, flinty, siliceous	0	11	
	Clay, plastic, light gray	1	8	
	Clay, light, siliceous	1	9	Lower
	Clay, dark, somewhat shaly	1	8	Mercer
	Clay, light, siliceous, hard	3	1	
	Clay, light, plastic	1	2	

Mogadore, Ohio.

The mines are located at Mogadore, Summit County, on the W. & L. E. R. R. The sample, designated "D," was taken from a large pile of unweathered clay representing 15 rooms in the mine. A vertical section is as follows:

		Ft.	In.
	Shale, dark	6	0
	Coal, smutty	0	1
Sample "D"	Clay, siliceous, gray	4	6
	Shale, dark, argillaceous	1	0

Lower Kittanning Clay, Toronto, Ohio.

The lower Kittanning clay, designated "E," is from the mine of the Toronto Fire Clay Co., Toronto, Jefferson County, and was sampled under covering. The sample is a representative one from different rooms in the mine. A vertical section of the mine is as follows:

		Ft.	In.
	Shale	15	0
	Coal, Lower Kittanning	2	6
Sample "E"	Clay (lower part siliceous)	7	0
	Clay, very siliceous, hard, gray	5	0
	Clay, bluish, sandy	2	0

Lower Kittanning Clays, New Brighton, Pa.

The clay, designated "F," was taken from a large pile of the Lower Kittanning clay at the Sherwood Bros. Pottery, New Brighton, Pa. This sample came from under cover and the section is similar to that at the mine of the A. F. Smith Co., both being Lower Kittanning clays occurring directly under the Lower Kittanning coal. The clay at the A. F. Smith Co. plant at New Brighton, is exposed and therefore is more weathered than that at the Sherwood Bros. Pottery. A vertical section of both mines is as follows:

		Ft.	In.
	Coal, Lower Kittanning	0	1
Samples "F" and "G"	Gray, plastic	5	0

Tionesta Clay, Crooksville, Ohio.

The sample designated "H," was taken from the mine of W. H. Brown and S. H. Sharky, located one mile west of Crooksville, Perry County. This clay is mined by drifting and is used extensively in both whiteware and stoneware potteries. The sample was taken from well under cover and from a clean face. The clay from this mine is shipped principally to the A. E. Hull Pottery. A vertical section is as follows:

		Ft.	In.
	Shale	5	0
	Limestone, Putman Hill	1	8
	Coal, Brookville	0	4
	Clay, light, plastic	6	0
	Clay, dark, carbonaceous, horizon of Tionesta	0	2
Sample "H"	Clay, light, plastic	6	0

Lower Kittanning Clay, Firebrick, Ohio.

The Lower Kittanning clay, designated "I," is used extensively in the manufacture of fire brick and sewer pipe in the southern

part of Lawrence County. The sample was taken from an open cut mine at Firebrick, Lawrence County. The bed is unusually free from nodules or sulphur compounds. A vertical section is as follows:

		Ft.	In.	
	Sandstone	8	0	
	Clay, shaly, Oak Hill	2	0	
	Coal	1	8	Lower Kittanning
	Clay	0	1½	Lower Kittanning
	Coal	0	8	Lower Kittanning
	Clay, dark, carbonaceous	0	4	
Sample "I"	Clay, light, plastic	5	0	
	Clay, siliceous, light	2	0	

Lower Kittanning Clay, Nelsonville, Ohio.

The Lower Kittanning clay, designated "J," is used extensively in the manufacture of brick at Nelsonville, Hocking County, and the sample was taken from the mine of the Hocking Valley Fire Brick Co., where it is used in the production of salt glazed building brick. A vertical section of the mine is as follows:

		Ft.	In.
	Sandstone	x	0
	Shale	6	0
	Coal, Lower Kittanning	1	8
	Clay, dark, carbonaceous	0	4
Sample "J"	Clay, light, plastic	8	6
	Sandstone, shaly	5	0

Semi-flint Clay, Scioto Furnace, Ohio.

The semi-flint clay, designated "K," was taken from a large pile at the plant of the Buckeye Fire Brick and Clay Co., Scioto Furnace, Scioto County. The clay is used extensively in the manufacture of high grade fire brick. A vertical section of the mine is as follows:

		Ft.	In.
	Shale	3	0
	Coal, Anthony	0	1
	Clay, flint	2	0
Sample "K"	Clay, semi-flint, Sciotoville	1	6
	Clay, "pink eye"	2	0

INVESTIGATION.

For the purposes of the investigation test pieces were molded from seven bodies which were prepared from each of the stoneware clays as follows:

Body No. 1—Run of mine clay ground dry to pass a 20-mesh sieve.
Body No. 2—Clay washed through a 150-mesh sieve.
Body No. 3—Residues from the washing were ground to pass a 150-mesh sieve and then added to the washed clay.
Body No. 4—95 per cent. washed clay (150-mesh) and 5 per cent. feldspar.
Body No. 5—90 per cent. washed clay (150-mesh) and 10 per cent. feldspar.
Body No. 6—95 per cent. washed clay (150-mesh) and 10 per cent. feldspar + 0.16 per cent. $CaCO_3$.
Body No. 7—95 per cent. washed clay (150-mesh) and 5 per cent. feldspar + 6.1 per cent. $CaCO_3$. [1]

The drying shrinkage, water of plasticity, shrinkage water, pore water, rate of slaking in water, and the transverse strengths in the green condition were determined for each body.

The softening points of the clays were compared to those of Orton pyrometric cones. The apparent porosities and volume

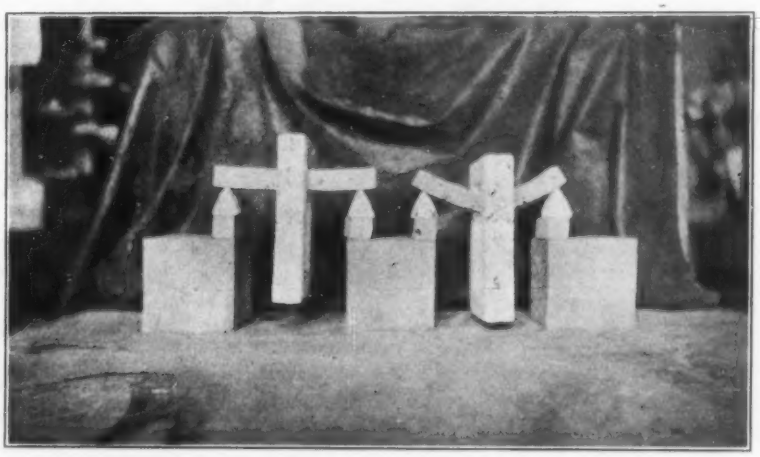

FIG. 1.—Clay bars before and after warpage test.

[1] Kirkpatrick, F. A., *Trans. Am. Ceram. Soc.*, **18**, 595 (1916). (The two calcite-orthoclase eutectics were used as a guide in adding the calcium carbonate.)

shrinkages of the briquettes were determined after firing to the different temperatures.

Owing to the fact that commercial chemical stoneware pieces are usually large, any tendency of the clays to warp, crack, or break in burning may cause high kiln losses. A modification of the warpage test as described by Worcester[1] was therefore employed—consisting in applying a load on the center of the

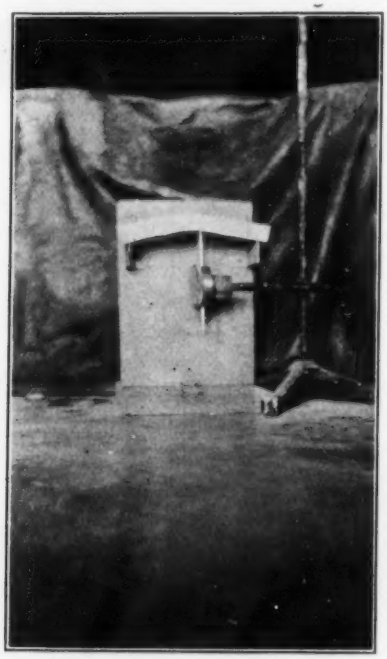

FIG. 2.—Method of measuring deformation with Ames dial.

test bars while resting upon two knife edges placed 6 inches apart, Fig. 1. A three-pound weight was applied to the bars having a $1'' \times 1''$ cross section, corrections being made for those having a smaller cross section. The deformation (Fig. 2) was expressed in per cent. warpage in terms of the length of the span.

[1] Worcester, W. G., *Trans. Am. Ceram. Soc.*, **12**, 818–853 (1910).

Transverse strength tests of the burned test bars were made after heating five times to 600° C and quenching in water at 18° C after each heating. The percentage decrease in strength gives a rough indication of the resistance of the fired bodies to temperature changes.

Results of the Tests.

Sample "A," Tionesta Clay, Ellis, Ohio.

This clay slakes down rapidly in water and is comparatively clean—leaving only 2.5 per cent. residue on the 150-mesh screen. It develops good mechanical strength in the raw and burned condition.

As all of the bodies investigated developed greater strength when burned to cone 8 than when burned to cones 6 or 10, it would appear that, for this class of clays and bodies, the maximum strength is developed by burning to cone 8. The difference in strength is probably due to underburning at cone 6 and overburning at cone 10. The strength of the clays and bodies is considerably increased by screening through the 150-mesh sieve.

The vitrification range is increased by screening through the 150-mesh sieve as compared with the run of mine clay screened through a 20-mesh sieve. The vitrification also starts about two cones lower. This is also true of the body in which the residue on the screen was ground to pass a 150-mesh sieve and then added to the washed clay. Screening the clay through a 150-mesh sieve also increases the burning shrinkage. Bodies Nos. 4, 5 and 6 have porosity and shrinkage curves which closely resemble that of the washed clay. Body No. 7 is comparatively open burning and has a short vitrification range. This is characteristic of high calcium bodies. The softening temperature is cone 26+ which roughly meets the requirements of a No. 3 fire clay as classified by Bleininger.[1]

The washed clay warps considerably under load. The run of mine clay, screened through the 20-mesh sieve, appears to be

[1] Bleininger, A. V., "Some Aspects of the Testing of Refractories," *Proc. Eng. Soc. Western Penn.*, **32**, 613 (1916).

more resistant to the quenching treatments than the same clay washed through a 150-mesh sieve.

Sample "B," Lower Kittanning Clay, Roseville, Ohio.

This clay slakes readily in water. Washing through a 150-mesh sieve affords a much "tighter" body than the run of mine clay screened through a 20-mesh sieve—as shown by a lower minimum porosity in the first case.

The softening point of this clay is cone 25+ and does not meet the requirements for a No. 1 fire clay. The clay warps considerably under load and therefore may be unsatisfactory if used alone.

Sample "C," Lower Mercer Clay, White Cottage, Ohio.

The clay does not slake readily in water and was therefore wet ground before blunging. The per cent. residue on a 150-mesh sieve is high. The strength of the raw clay is low while that of the burned clay is good. Adding the reground residue to the washed clay tends to open the body. The softening point, cone 26, would probably classify this material as a No. 2 fire clay. The warpage under load at cone 4 is excessive and high kiln losses may be expected if this clay is used alone in the manufacture of chemical stoneware.

Sample "D," Mogadore, Ohio.

This clay does not slake readily in water and was therefore wet ground before blunging. The per cent. residue on a 150-mesh sieve is high. The strength in the dry condition is low, although the burned strength is fair. The softening point is cone 18. The resistance of the test pieces, molded from the washed clay, to warpage under load, is not satisfactory.

Sample "E," Lower Kittanning Clay, Toronto, Ohio.

This clay does not slake in water and was therefore wet ground before blunging. The modulus of rupture of the test pieces from the washed clay is excellent while that of the clay when burned to cone 8 is also very good. The softening point is cone 26—roughly meeting the requirements for a No. 3 fire clay. The resistance to warpage under load is not very satisfactory.

Sample "F," Lower Kittanning Clay, New Brighton, Pa.

This clay slakes readily in water. The dry strength is low although the burned strength is fair. The softening point is cone 28—roughly meeting the requirements for a No. 2 fire clay. The resistance of the test pieces molded from the washed clay to warpage under load is poor.

Sample "G," Lower Kittanning Clay, New Brighton, Pa.

This clay slakes readily in water. The strength in the raw and burned condition is fair. The addition of the reground residue to the washed clay produces a more open body than the use of the washed clay alone. The softening point is cone 28, meeting the requirements for a No. 2 fire clay. The resistance to warpage under load at cone 4 is not satisfactory.

Sample "H," Tionesta Clay, Crooksville, Ohio.

This clay slakes readily in water. The dry strength is fair while the burned strength is good. The softening point is cone 28, which roughly meets the requirements of a No. 2 fire clay. The resistance to warpage under load is not very good.

Sample "I," Lower Kittanning Clay, Firebrick, Ohio.

This clay slakes readily in water. The strength in the dry and burned condition is excellent. The addition of feldspar to this clay is advisable as it widens and lowers the vitrification range by 4 cones. The color, when burned, is light gray and similar to that of the ball clays used in the manufacture of white ware. The softening point, cone 31, is sufficiently high to warrant the use of the clay in the manufacture of glass pots. The clay has only a small tendency to warp.

Sample "J," Lower Kittanning Clay, Nelsonville, Ohio.

This clay slakes readily in water. The per cent. residue remaining on the 150-mesh sieve is low. The strength in the dry and burned condition is excellent. The softening point, cone 30, classifies the material as a No. 2 fire clay. The resistance to warpage under load is fair.

Sample "K," Lower Kittanning Clay, Scioto Furnace, Ohio.

This clay does not slake readily in water and was therefore wet ground in a ball mill previous to blunging. The dry strength is low, although the burned strength is excellent. The softening point, cone 32+, classifies the material as a No. 1 fire clay. This clay is considered as being one of the typical fire-brick clays of Ohio. The resistance to cracking and warpage under load at cone 2 is very poor.

Summary.

With but few exceptions, the screening of the clays through a 150-mesh sieve improves the strength in the raw and burned condition, increases the dry porosity, lowers the vitrification temperature, widens the vitrification range, decreases the minimum burned porosity, increases the burning shrinkage, and increases the density in the burned condition.

When ground and screened to pass through a 150-mesh sieve, the residue from the washing may be added to the washed clay to advantage in most cases. The addition of feldspar alone or with a small percentage of calcium carbonate lowers the vitrification temperature. When a large percentage (6.1 per cent.) of calcium carbonate is added, the bodies are more porous at the lower temperatures, the vitrification temperature is raised, and in general the vitrification range is narrowed.

The maximum strength of all of the clays tested is developed by burning to cone 8.

There appears to be no relation between the softening temperature and the resistance to warpage under load at the low temperatures—the most refractory clays sometimes fail before the less refractory ones.

There is a large decrease in the mechanical strength when the clays are being burned above cone 1. In one case, the modulus of rupture was 270 in the dry state and, although the clay is a No. 1 fire clay, its modulus of rupture at cone 4 was decreased to 27.

The run of mine clays, screened dry through a 20-mesh sieve, appear to be more resistant to the quenching treatments than the same clays when screened through a 150-mesh sieve.

TABLE 1.—MISCELLANEOUS PROPERTIES.

No.	Per cent. residue on 150-mesh.	Per cent. porosity, dry.	Density, dry.	Modulus of rupture, lbs. per sq. in. (Dried 110° C).	Per cent. warpage. Cone 1.	Cone 2.	Cone 4.	Loss of strength due to quenching treatment. (Per cent.)	Softening points. (Cones.)
1A.....	2.5	27.0	1.90	389.5	...	...	...	91.5	26+
2A.....	...	29.6	1.83	467.9	0.83	2.42	8.95	96.3	...
1B.....	6.1	23.8	2.06	218.6	...	...	...	77.5	26+
2B.....	...	28.1	1.87	319.5	2.77	5.13	9.99	97.7	...
1C.....	9.4	23.6	1.96	132.0	...	...	...	77.6	26
2C.....	...	25.7	1.80	250.7	2.75	6.10	15.10	93.0	...
1D.....	12.0	23.2	2.02	142.5	...	...	...	82.0	18
2D.....	...	28.5	1.87	259.0	1.80	3.48	6.40	93.0	...
1E.....	7.0	19.4	2.10	384.3	...	...	...	78.6	26—
2E.....	...	27.2	1.90	532.1	2.48	2.75	6.44	92.0	...
1F.....	9.4	23.4	1.99	194.2	...	...	...	82.5	28
2F.....	...	29.7	1.79	191.0	3.58	5.91	10.70	96.0	...
1G.....	12.5	24.5	1.94	194.5	...	...	...	83.5	28
2G.....	...	27.9	1.88	321.0	2.58	3.22	6.70	94.0	...
1H.....	7.2	23.1	1.98	178.8	...	...	...	73.5	28
2H.....	...	29.0	1.83	314.9	3.30	3.89	7.50	93.5	...
1I.....	1.2	24.8	1.89	324.9	...	...	...	85.5	31
2I.....	...	25.6	1.91	499.2	0.83	0.84	3.80	96.5	...
1J.....	3.4	20.8	2.04	247.3	...	...	...	77.5	30
2J.....	...	29.2	1.86	350.1	0.58	...	5.80	95.0	...
1K.....	5.0	18.5	2.03	93.8	...	...	...	55.5	32+
2K.....	...	28.4	1.88	270.0	0.58	8.85	broke	95.4	...

TABLE 2.—PER CENT. APPARENT POROSITIES OF CLAYS AND MIXTURES BURNED TO DIFFERENT TEMPERATURES.

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.	Cone 14.
1A.....	19.38	15.90	3.70	0.78	0.93	0.20	2.20	...
2A.....	17.58	15.88	0.14	0.28	0.36	0.23	4.00	1.72
3A.....	19.28	16.10	0.14	0.21	0.36	0.16	1.50	1.59
4A.....	19.10	14.50	0.54	0.12	0.01	0.06	3.90	2.47
5A.....	19.05	14.65	0.14	0.17	0.08	0.09	0.35	3.70
6A.....	18.80	14.10	0.03	0.06	0.15	0.00	0.16	3.46
7A.....	24.85	19.80	6.49	1.07	5.99	...	5.70	3.39

TABLE 2.—(*Continued*).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.	Cone 14.
1B.....	18.93	17.15	12.99	12.79	12.48	14.80	12.80	5.20
2B.....	20.60	14.15	0.91	0.24	4.97	3.20	6.30	...
3B.....	21.45	14.60	0.24	0.94	3.99	1.04	6.80	...
4B.....	16.75	15.50	0.34	0.15	2.03	0.78	4.60	4.35
5B.....	17.50	14.65	0.12	0.12	4.77	0.60	6.40	...
6B.....	17.15	14.28	0.99	0.24	2.21	2.18	5.00	...
7B.....	23.15	23.15	15.90	6.00	0.28	0.00	5.50	...
1C.....	19.60	22.80	14.55	10.40	7.32	4.95	5.10	8.50
2C.....	19.90	18.50	6.59	2.75	0.78	1.45	6.10	8.31
3C.....	24.00	24.10	12.65	9.00	1.31	4.41	6.70	9.68
4C.....	21.55	21.35	10.25	4.30	1.93	2.34	3.60	8.72
5C.....	22.00	18.35	9.70	4.60	2.09	1.54	6.00	6.50
6C.....	22.05	21.25	10.33	3.75	0.59	2.94	6.00	7.40
7C.....	28.63	29.20	18.10	8.00	0.22	0.00	7.00	...
1D.....	24.75	25.25	18.80	15.30	12.12	7.33	4.80	5.65
2D.....	22.55	23.60	17.50	9.40	3.63	3.37	3.37	11.70
3D.....	27.48	26.30	19.00	10.60	2.92	2.75	6.20	10.48
4D.....	23.15	23.55	16.20	4.30	2.93	2.17	8.60	10.20
5D.....	24.35	22.30	7.73	7.50	2.49	2.29	9.80	6.12
6D.....	22.85	22.85	9.33	8.88	2.44	1.55	9.00	7.37
7D.....	29.05	30.30	14.23	11.53	9.35	9.30	19.00	...
1E.....	22.20	19.75	10.74	10.88	10.93	10.51	11.00	10.70
2E.....	24.30	20.25	7.43	4.00	3.25	7.80	8.80	8.72
3E.....	24.70	19.83	6.50	3.00	2.21	6.95	8.50	10.40
4E.....	24.90	20.55	8.60	2.50	0.23	11.70	6.20	...
5E.....	21.20	17.60	5.98	1.00	5.69	5.82	9.20	...
6E.....	24.80	21.00	11.69	4.50	2.46	12.10	6.30	2.41
7E.....	23.65	23.15	14.25	5.75	0.06	0.00	7.90	8.20
1F.....	20.20	23.40	16.58	14.25	13.24	12.45	7.50	2.44
2F.....	24.95	25.05	11.00	3.75	1.03	5.57	6.40	6.68
3F.....	25.60	27.00	13.70	5.40	3.31	3.71	5.10	5.58
4F.....	21.90	24.55	7.89	4.00	2.58	6.88	10.30	3.00
5F.....	23.55	25.20	6.36	4.00	4.44	4.88	9.80	2.77
6F.....	20.75	24.30	8.33	2.50	0.29	1.84	3.50	2.90
7F.....	27.35	31.65	14.35	4.00	0.08	0.28	1.70	...
1G.....	21.95	22.95	20.00	15.00	10.32	9.60	5.20	10.85
2G.....	21.35	19.85	16.00	5.00	1.80	7.49	8.00	11.20
3G.....	23.00	21.95	18.00	8.75	3.02	5.60	7.10	12.60
4G.....	21.00	18.75	14.00	2.80	0.39	0.26	4.10	10.90
5G.....	22.30	18.95	14.00	4.00	1.15	5.23	6.60	5.09
6G.....	24.00	21.20	12.50	5.00	0.73	6.55	8.10	11.45
7G.....	27.00	26.70	15.95	4.00	0.33	0.18	9.40	...

TABLE 2.—(*Continued*).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.	Cone 14.
1H.....	24.95	22.95	17.80	16.00	14.50	11.40	10.00	5.48
2H.....	26.75	22.00	16.20	5.50	0.25	3.30	0.59	7.95
3H.....	25.00	19.10	14.58	10.60	6.68	4.14	1.79	2.42
4H.....	25.65	21.20	7.85	2.00	0.37	0.00	4.20	...
5H.....	22.75	18.00	7.98	1.75	0.41	0.17	5.30	7.56
6H.....	24.00	21.20	10.23	2.50	0.35	0.29	0.59	6.31
7H.....	27.00	26.70	15.95	4.50	0.29	0.24	0.78	...
1I.....	19.15	19.10	16.23	12.00	10.78	7.84	6.30	6.64
2I.....	18.23	19.40	11.95	7.25	5.23	4.55	0.17	8.50
3I.....	19.65	19.10	12.55	7.75	5.54	4.74	1.30	8.90
4I.....	18.30	17.55	9.29	3.75	0.61	0.45	1.80	5.04
5I.....	14.48	13.40	5.89	1.90	0.08	0.01	2.70	3.91
6I.....	16.20	15.30	10.10	4.75	0.33	1.15	0.49	4.52
7I.....	16.70	14.65	13.27	8.50	3.22	0.12	0.00	9.10
1J.....	21.75	18.95	15.01	12.10	10.66	10.45	8.30	...
2J.....	24.20	21.75	12.40	3.00	0.08	0.43	1.06	5.77
3J.....	24.95	21.55	12.30	4.75	0.23	0.32	3.60	8.71
4J.....	22.80	18.20	10.70	2.60	0.09	0.19	0.73	7.43
5J.....	22.85	17.30	9.80	2.25	0.09	0.12	3.30	7.85
6J.....	22.90	18.70	9.60	2.25	0.09	0.13	3.31	7.40
7J.....	27.00	27.15	17.45	7.00	0.12	0.05	0.02	10.70
1K.....	23.85	20.85	22.50	22.80	21.65	19.10	17.20	18.15
2K.....	21.65	18.55	14.07	9.75	8.70	8.40	2.30	2.85
3K.....	25.30	19.65	18.73	12.50	11.25	10.70	5.25	3.57
4K.....	22.90	16.15	12.98	9.00	6.65	5.67	1.60	3.42
5K.....	21.70	14.50	11.66	7.50	2.95	1.49	4.72	1.90
6K.....	20.55	15.30	9.53	8.00	6.47	5.38	0.00	1.81
7K.....	16.35	17.25	15.65	12.00	10.14	8.82	0.15	1.53

TABLE 3.—MODULUS OF RUPTURE OF BURNED BODIES.

No.	Cone 6.	Cone 8.	Cone 10.
1A.....	4624.0	6680.0	3812.0
2A.....	7200.0	8265.0	5330.0
3A.....	7240.0	10747.0	4671.0
4A.....	6538.0	7780.0	4910.0
5A.....	6540.0	6787.0	5966.0
6A.....	6616.0	8728.6	6001.0
7A.....	5566.0	6958.3	5779.0

TABLE 3.—(*Continued*).

No.	Cone 6.	Cone 8.	Cone 10.
1B	3190.0	3416.2	2665.0
2B	8556.0	8680.0	7504.8
3B	7628.0	9505.0	9462.0
4B	8130.0	9738.3	6911.6
5B	7010.0	8482.9	7050.0
6B	6957.0	7514.0	6494.0
7B	5434.0	6003.7	4853.0
1C	2964.0	3223.7	1670.0
2C	5703.0	7285.0	4681.0
3C	4534.0	6485.0	4543.0
4C	5254.0	5843.7	4421.0
5C	5491.0	7802.5	4749.0
6C	4564.0	5090.0	4321.0
7C	4090.0	7067.1	3464.0
1D	2023.0	2283.7	2181.0
2D	4666.0	4820.0	3361.0
3D	3686.0	4585.0	2418.0
4D	4284.0	5581.4	3326.0
5D	4621.0	5790.0	2991.0
6D	4606.2	5877.5	3944.0
7D	3944.3	4627.5	2218.0
1E	2788.7	3568.7	2260.0
2E	7904.3	6847.5	5690.0
3E	.....	.....	....
4E	5882.8	6397.5	5084.0
5E	5128.6	5191.6	4584.0
6E	5430.0	5588.5	4155.0
7E	5168.7	5385.0	4873.0
1F	2911.2	3063.0	1909.0
2F	4932.5	5815.0	3368.0
3F	4213.8	5133.0	3750.0
4F	4472.5	5507.0	3869.0
5F	6275.0	6727.0	2675.0
6F	4751.4	6059.0	3260.0
7F	3908.7	5309.0	2057.0
1G	2580.0	3288.7	1521.0
2G	5113.0	5183.7	4474.0
3G	4948.7	6350.0	2643.0
4G	4993.8	5473.0	5400.0
5G	4853.7	6284.0	4506.0
6G	4973.0	5780.0	4381.0
7G	3715.0	5890.0	4545.0

TABLE 3.—(*Continued*).

No.	Cone 6.	Cone 8.	Cone 10.
1H	1974.0	3043.7	1956.0
2H	6615.0	7148.7	3689.0
3H	2873.3	6837.0	1912.0
4H	5682.0	7960.0	4586.0
5H	6111.2	9075.0	3941.0
6H	6591.2	7768.5	5535.0
7H	5058.7	6208.7	3682.0
1I	4068.7	5075.0	3014.5
2I	10448.3	7190.0	6175 6
3I	.....	9438.0	6073.0
4I	7045.0	9691.0	7023.0
5I	6734.0	7227.5	7207.0
6I	6847.1	8837.1	7238.0
7I	5561.0	6052.9	5169.0
1J	1569.0	3507.5	2034.0
2J	4699.0	6150.0	5004.0
3J	5619.0	6522.5	4125.0
4J	5523.0	8640.0	4018.0
5J	6404.0	6635.0	5799.0
6J	6165.0	8481.2	5850.0
7J	5561.4	6221.1	4528.0
1K	1649.4	2129.3	2041.0
2K	3655.0	7411.0	2716.0
3K	3730.0	8976.0	3201.0
4K	2836.6	5742.0	3546.0
5K	3585.0	4710.0	3567.0
6K	2235.0	8740.0	2046.0
7K	2437.8	5621.2	5064.0

TABLE 4.—PER CENT. VOLUME SHRINKAGE OF CLAYS AND MIXTURES BURNED TO DIFFERENT TEMPERATURES.

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.
1A	13.20	15.90	24.00	24.31	23.30	24.90	...
2A	19.80	21.10	29.55	29.50	28.80	29.10	21.80
3A	20.90	22.05	30.85	32.25	32.35	32.55	28.10
4A	17.95	20.83	28.09	30.25	35.60	28.00	...
5A	17.53	19.35	27.41	28.75	28.85	28.85	25.80
6A	21.15	23.80	30.64	31.60	31.45	31.55	28.50
7A	13.85	14.85	24.44	23.51	17.20	...	22.90

TABLE 4.—(*Continued*).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.
1B	14.40	14.70	17.12	16.53	9.06	8.63	6.30
2B	20.45	25.05	32.30	31.19	24.80	...	41.25
3B	21.85	25.65	32.40	34.58	26.60	...	33.95
4B	19.75	22.60	29.00	28.73	26.80	...	22.20
5B	15.10	20.65	27.13	27.48	22.40	22.80	27.20
6B	20.00	22.45	29.18	28.80	24.15	...	31.60
7B	14.50	15.80	19.24	21.70	24.80	...	24.60
1C	7.43	8.36	15.14	16.25	16.40	16.40	13.70
2C	16.15	20.25	26.75	27.95	28.40	26.80	19.35
3C	10.08	13.89	20.88	26.65	28.40	23.80	20.60
4C	12.60	14.87	22.10	24.25	24.85	24.65	23.75
5C	12.83	18.00	18.50	25.36	23.55	23.10	17.30
6C	12.23	15.12	20.70	24.25	27.35	23.40	19.50
7C	6.10	7.66	16.15	22.50	25.75	25.90	14.30
1D	3.70	5.98	6.92	7.95	9.00	10.90	14.10
2D	8.43	8.64	17.85	18.96	23.45	23.40	19.80
3D	5.86	8.51	18.13	20.75	24.90	25.00	20.50
4D	8.18	9.36	17.48	18.30	23.40	23.40	14.50
5D	8.55	10.98	19.38	20.95	22.4	22.30	5.40
6D	8.33	7.82	16.53	19.00	23.65	23.60	9.00
7D	2.93	3.54	15.03	19.95	21.97	20.03	19.00
1E	7.14	8.60	15.03	9.43	6.06	5.57	4.60
2E	10.64	15.87	23.50	22.70	21.90	20.60	15.90
3E	10.85	15.21	24.80	24.65	24.80	22.40	17.60
4E	11.55	14.65	22.85	24.00	25.55	23.00	20.30
5E	14.40	15.47	24.55	25.70	20.35	18.30	14.10
6E	10.45	14.19	21.88	23.65	23.35	...	16.75
7E	10.02	13.56	14.28	16.78	23.00	23.50	13.30
1F	3.64	5.92	8.25	9.42	12.43	11.95	7.50
2F	9.23	12.85	19.00	22.00	28.65	22.93	3.40
3F	8.10	11.36	16.25	20.00	28.25	27.75	5.10
4F	11.28	14.03	20.00	25.69	24.40	19.20	10.30
5F	9.23	13.96	20.00	26.38	22.15	20.25	9.80
6F	9.78	13.17	13.25	24.65	28.15	27.80	3.50
7F	5.93	8.28	12.00	20.03	28.45	29.40	1.70
1G	6.48	7.37	14.00	14.40	17.50	20.20	18.00
2G	9.49	16.74	20.20	24.00	26.60	23.00	20.60
3G	8.53	9.93	18.10	24.30	25.90	23.45	23.20
4G	9.73	14.96	20.55	24.00	26.55	22.95	16.33
5G	11.68	15.63	24.30	26.00	25.40	22.70	15.45
6G	10.78	14.50	21.70	26.60	26.85	22.00	18.45
7G	5.59	8.05	17.65	22.75	25.40	25.55	12.40

TABLE 4.—(*Continued*).

No.	Cone 1.	Cone 2.	Cone 4.	Cone 6.	Cone 8.	Cone 10.	Cone 12.
1H	6.63	8.32	11.35	13.00	13.70	13.43	13.10
2H	13.88	16.52	23.55	23.00	28.55	33.40	...
3H	15.00	16.68	29.70	32.00	32.85	33.00	34.00
4H	12.70	16.36	25.35	26.40	27.10	27.30	21.00
5H	13.45	18.54	25.00	27.30	26.80	27.00	19.00
6H	13.55	16.87	23.00	27.00	28.80	28.85	28.60
7H	9.60	11.44	18.15	25.00	28.20	28.20	24.80
1I	13.63	15.03	16.80	19.60	20.40	20.65	22.00
2I	17.75	19.40	22.30	25.00	25.75	25.95	26.40
3I	17.53	17.71	21.55	22.00	22.00	22.70	27.80
4I	14.30	16.38	21.00	24.00	24.25	22.80	...
5I	19.17	21.40	24.20	25.70	26.25	28.60	15.00
6I	19.10	20.98	24.05	27.00	28.15	27.70	...
7I	9.60	11.44	18.15	22.50	24.60	26.90	22.90
1J	9.78	10.96	13.30	12.10	10.10	10.10	7.50
2J	13.73	16.40	22.45	29.00	30.10	29.90	28.90
3J	14.90	16.91	22.80	28.50	29.70	29.00	23.70
4J	13.60	18.23	23.55	29.00	30.45	30.40	28.00
5J	15.50	18.55	24.00	28.10	29.25	29.50	21.10
6J	15.90	17.84	25.15	29.50	30.30	31.90	25.60
7J	7.32	8.45	14.50	22.00	26.10	26.30	25.50
1K	15.40	16.59	18.40	20.25	20.90	18.88	17.10
2K	23.05	25.15	28.90	31.25	32.00	32.30	33.40
3K	21.40	23.28	24.90	27.50	30.45	30.85	33.55
4K	22.75	27.63	30.10	32.00	33.55	34.15	35.60
5K	23.20	28.78	30.10	32.00	34.10	34.75	35.30
6K	20.80	26.18	28.20	30.50	32.15	32.60	34.00
7K	...	23.70	23.80	26.00	28.30	28.50	30.15

TABLE 5.—SHRINKAGE RELATIONS.

No.	Description.	Per cent. total water in terms of true clay volume.	Per cent. shrinkage water in terms of true clay volume.	Per cent. pore water in terms of true clay volume.	Ratio of per cent. pore water to per cent. shrinkage water.	Per cent. shrinkage water in terms of total water.	Per cent. water of plasticity in terms of dry weight.	Per cent. volume shrinkage in terms of dry volume.
1A	Run of mine	78.8	41.7	37.3	0.92	52.9	30.3	30.5
2A	Washed	83.9	44.0	39.9	0.91	52.4	34.2	33.2
1B	Run of mine	71.3	40.3	31.0	0.77	56.5	27.5	30.8
2B	Washed	90.6	48.5	42.1	0.87	53.5	34.8	33.0

TABLE 5.—(*Continued*).

No.	Description.	Per cent. total water in terms of true clay volume.	Per cent. shrinkage water in terms of true clay volume.	Per cent. pore water in terms of true clay volume.	Ratio of per cent. pore water to per cent. shrinkage water.	Per cent. shrinkage water in terms of total water.	Per cent. water of plasticity in terms of dry weight.	Per cent. volume shrinkage in terms of dry volume.
1C	Run of mine.....	61.1	30.2	30.9	1.02	49.5	23.5	22.9
2C	Washed.....	81.6	38.3	43.3	1.13	46.9	31.4	26.6
1D	Run of mine.....	49.8	20.8	29.0	1.40	41.7	19.1	16.1
2D	Washed.....	75.0	37.1	37.9	1.02	49.5	28.9	26.7
1E	Rune of mine	49.0	23.5	25.5	1.07	48.0	18.9	18.9
2E	Washed.....	86.3	50.5	35.8	0.71	58.5	33.2	36.2
1F	Run of mine.....	54.6	26.0	28.6	1.19	47.5	21.0	20.0
2F	Washed.....	83.8	38.8	45.0	1.16	46.3	32.2	26.4
1G	Run of mine.....	64.5	33.7	30.8	0.91	52.2	24.8	25.1
2G	Washed.....	76.0	39.8	36.2	0.91	52.3	29.2	27.4
1H	Run of mine.....	63.1	29.8	33.3	1.12	47.1	24.3	22.7
2H	Washed.....	88.0	46.0	42.0	0.91	52.3	33.8	32.3
1I	Run of mine.....	88.5	56.0	32.5	0.58	63.3	34.2	40.6
2I	Washed.....	89.6	55.6	34.0	0.61	62.0	34.6	41.2
1J	Run of mine.....	59.6	30.6	29.0	0.95	51.3	23.0	22.7
2J	Washed.....	87.6	48.5	39.1	0.81	55.4	33.7	34.7
1K	Run of mine.....	43.5	17.8	25.7	1.44	41.0	16.8	14.0
2K	Washed.....	86.0	48.0	38.0	0.79	55.8	33.1	34.6

The properties of the above Ohio and Pennsylvania stoneware clays were studied by the Bureau of Mines under the direction of Prof. A. S. Watts in coöperation with the Ohio Geological Survey. The Pennsylvania Geological Survey also assisted in obtaining the Pennsylvania stoneware clay samples. Although this work was done with special reference to chemical stoneware, many results were brought out which may be applied to a number of other ceramic industries.

THE USE OF DENSE SOLUTIONS IN DETERMINING THE STRUCTURE OF PORCELAINS.

By H. Spurrier, Detroit, Mich.

Petrographers and mineralogists have used dense organic and inorganic solutions for a number of years in the separation of minerals having different specific gravities. Under certain conditions fused solids have also been used.

The use of a dense solution in the grading of porcelains was suggested by the variations in specific gravity encountered in underfired, properly fired and overfired spark plug insulators. A slightly underfired piece of porcelain has a higher specific gravity than a properly fired piece of the same composition while the specific gravity of an overfired piece is less than that of a properly fired piece.

In an attempt to determine the reliability and accuracy of a visual inspection of porcelains the following tests were made:

Four pieces of porcelain were selected and visually classified by a competent inspector. Two of the pieces were rejected by him as being overfired and two were passed as being properly fired. However, one of the pieces selected as being properly fired showed a tendency toward slight overfiring. Upon submitting the same four pieces to another inspector, he classified them in the same way, confirming the judgment of the first inspector.

Careful specific gravity determinations on the four pieces gave the following results:

Classification (inspector).	Sp. Gr.
Overfired	1.865
"	1.861
Properly fired	2.086
" "	1.916

The piece having a specific gravity of 1.916 was the one in regard to which there was a slight question as to its being properly

fired. It is apparent, therefore, that visual examination by skillful inspectors is not all that could be desired in the selection of the properly fired porcelains.

For the rapid laboratory or factory testing of porcelains by means of heavy solutions, a liquid having the following properties is necessary:

1. The specific gravity should be 2.3 or above.
2. The liquid should be mobile at the necessary concentrations.
3. It should not exert a corrosive action on the material being tested.
4. It should be fairly constant in specific gravity.
5. It should be available in commercial quantities at reasonable cost.

In endeavoring to find a liquid which would be suitable for the specific-gravity determinations on porcelains, the following observations were made in reference to some of the solutions used by mineralogists:

Acetylene tetrabromide can be diluted only with ether or benzol and is therefore somewhat unstable as to specific gravity.

Methylene iodide is easily decomposed by light.

Klein's solution, cadmium borotungstate, is prepared with considerable difficulty.

The specific gravity of concentrated zinc chloride (82.12 per cent. $ZnCl_2$, 17.88 H_2O) is 2.2307. At the desired concentration, however, it is quite viscous.

Potassium mercuric iodide meets all of the requirements of a liquid to be used for this purpose but is quite expensive.

Acid nitrate of mercury is quite mobile and remarkably stable and appears to have all of the desirable properties enumerated above.

In the grading of porcelains in our laboratory by means of the acid mercuric nitrate, two solutions are used, the one being diluted so as to just float a properly fired piece and to allow an underfired piece to sink—the other being so diluted as to allow a properly fired piece to sink and an overfired piece to float. The solutions may become a little too dense with age but this is remedied by the addition of a little water acidified with nitric acid.

The density of the solution, when once established for a certain body, should be checked from time to time by means of a good specific gravity hydrometer. Upon removing and washing the tested pieces with water, a yellow deposit will occur but this can be easily removed with a little acetic acid.

It is, of course, quite obvious that the specific gravity of fired ware may vary quite sensibly in consequence of the presence of mechanical voids, and that a properly fired piece of ware may possess an apparent specific gravity below the established standards. In such cases the ware is rejected by the solution. This is as it should be where careful selection of the porcelains is necessary. The fact that invisible imperfections in the porcelains are at once detected by this method makes it more efficient than visual examination by the inspector.

We have used a solution of the acid mercuric nitrate only as a rapid laboratory check for the insulator inspectors but its use offers interesting possibilities as an exact method for factory testing.

By the employment of this method, one more operation is relieved of the uncertain personal factor and placed upon an unvarying mathematical basis.

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DISCUSSION.

MR. MCDOUGAL: I would like to ask Mr. Spurrier if he has found that a difference in the thickness of the glaze on a spark plug insulator would be an important factor in the employment of this test; that is, would a heavier glaze on one piece affect the apparent specific gravity so as to indicate an apparently denser structure than that of a piece having a lighter glaze coating?

MR. SPURRIER: A glaze usually has a higher specific gravity than the body to which it is applied, and if the glaze area is very large, in proportion to the volume of the porcelain, it will be a source of error in the specific gravity determination. The glaze, if uniform, is usually so thin that, within the necessary limits, it does not affect the behavior of the piece in the solution.

MR. CREIGHTON: This method, in its simplicity, appeals to me very greatly. I should like to ask Mr. Spurrier if the size of the piece is not an important factor to be considered, and also if the character of the surface of the piece, whether rough or smooth, will not affect the results? If the surface of the piece is rough, will not a certain amount of air be trapped when the piece is dropped into the solution—thus affecting the reading? If the piece is large the importance of this factor would be diminished.

MR. SPURRIER: In making specific-gravity determinations in water great care is necessary to prevent the entrapping of air by the piece being tested. I have found, however, that by exercising reasonable care, no difficulties from entrapped air are encountered in the testing of the porcelain pieces in the dense solutions.

MR. WATTS: I would like to ask Mr. Spurrier whether—in the use of these solutions—there would be any objection to placing the porcelains in a metal gauze basket while inserting into the solutions? Are the solutions corrosive to metals—nickel, etc.?

MR. SPURRIER: Yes, the dilute nitric acid, but some of the high silica irons now available are particularly resistant to nitric acid and the mercury does not affect them.

MR. WATTS: That is just the point I wanted to raise: would a small amount of the metal that might be taken up from the basket materially affect the density of the solution?

MR. SPURRIER: No, I think not, because the volume of the liquid is large in proportion to the volume of the pieces being tested.

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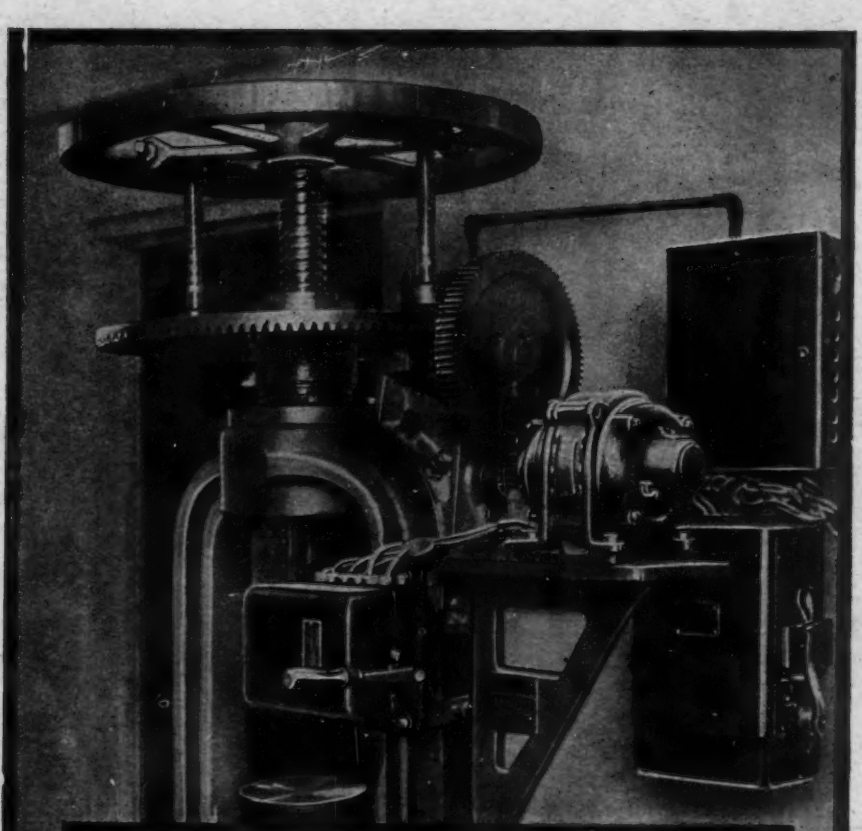

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